The European Dioxin Emission Inventory
Stage II

Volume 2

Desktop studies and case studies

This report was prepared by the North Rhine Westphalia State Environment Agency on behalf of the European Commission, Directorate General for Environment (DG ENV)

Contract No.:	96/771/3040/DEB/E1
Contract period:	01.01.1998 – 31.12. 2000
Release date:	31.12.2000
Authors:	Ulrich Quass, Michael Fermann, Günter Bröker

Title	The European Dioxin Emission Inventory, Stage II
Customer	European Commission, Directorate General for Environment (DG ENV)
File reference	Deckblatt Band2.doc; Chap01_ Overview.doc; Chap02_ DomBurnConcept.doc; Chap03_ LandWaterEmissions.doc; Chap04_ Inventory_ France.doc; Chap05_ CentralEurope.doc; Chap06_ ClinWasteInc.doc; Chap07_ Sinter.doc; Chap08_ CupolaFoundries.doc; Chap09_ TiO2.doc; Chap10_ SulfurDioxins.doc; Chap11_ DieselEngines.doc; Chap12_ DomBurnCoal.doc; Chap13_ Greece.doc; Chap14_ Portugal.doc; Glossar.doc; Annex1.doc; Annex2.doc
Report number	Volume 2
Report status	Final Report – December 2000

Project leader/contact

Prof. Dr. Günter Bröker
Landesumweltamt NRW
Wallneyer Str. 6
45133 Essen
Nordrhein-Westfalen
Germany
Telephone +49 (0)201 7995-1260
Facsimile +49 (0)201 7995-1446 / 1447 / 1575

	Name	Signature	Date
Authors	Ulrich Quass		
	Michael Fermann		
	Günter Bröker		

Content of Volume 2

1. Introduction and overview

1.1 Background

During the execution of Stage I of this project from 1995 to 1997 it soon became evident that for a number of emission source types as well as for some of the European Countries data on PCDD/F emissions were scarcely obtainable. Hence, it was decided at a quite early stage to carry out a follow-up project which mainly should be directed toward gathering of additional information about the most relevant sources and obtaining first measuring results from countries where no information had been available for the Stage I report.

Environmental authorities and experienced public and private institutes were invited to participate in the Stage II project. In November 1997 a workshop was held at LUA, Essen with delegates from those institutions which responded positively. The objective of this workshop was to discuss the Stage I results and to decide on the actions mostly needed to improve the situation concerning the identified data gaps. The results of this workshop can be summarised as follows:

- In spite of being highly relevant for the annual PCDD/F emissions to air no further activity within Stage II was to be directed to municipal solid waste incineration because the state of information was already considered as satisfying. Moreover, it was expected that ongoing legislative processes in the European Union would lead to a general emission limit of 0.1 ng I-TEQ/m³ for these facilities within short time.

- The information on dioxin emission factors for domestic heating facilities was considered as limited and an urgent need to improve this data base was identified. However, comprehensive measurement programmes to generate more knowledge were assessed to be far beyond the scope of the Stage II project. Hence it was decided to ask some of the institutions particularly being interested in this topic to evaluate the existing information and to prepare a report on further research needed.

- Considerable lack of information was identified with respect to emissions of dioxins and furans to Land and water (via waste water streams and solid/liquid production residues being deposited). A desktop study on this subject therefore was requested which should be complementary to the Stage I report which mainly focused on emissions to air.

- Emission measurements should be done in various countries at industrial facilities which were assessed to be highly relevant and/or for which insufficient information could be obtained so far. A ranking list of source types was agreed on, which should be taken as a basis for establishing corresponding sub-projects between LUA and interested institutes. Based on this relevance list a number of sub-projects were outlined which in the following should be negotiated on in detail.

However, the scope and the likelihood of realisation of these sub-projects depended on the availability of experienced laboratories in the countries of interest, on the accessibility of plants and on financial background conditions. Quite frequently lengthy negotiations between all parties involved were necessary which at the end led to cancellation of a project in some cases. The following sub-projects were carried out within Stage II:

1.2 Sub-projects and measurement programmes of Stage II

1.2.1. Desktop studies

- A comprehensive study on dioxin emissions to land and water prepared by AEA Technology, plc in the United Kingdom which completes the Stage I report.
- Under leadership of the Austrian Institute FTU (Forschungsgesellschaft Technischer Umweltschutz) and in collaboration with institutes located in The Netherlands, Norway and Denmark a proposal was made for a research project on the subject of dioxin emissions from domestic wood and coal burning in the European countries.
- Carried out independently of the Stage II project, the French dioxin inventory is included into this report as a further “desk top-study” because this inventory provides important information on a number of emission source types
- Finally, through contacts with experts and environmental institutes in some of the accession countries, data on dioxin emission sources in Poland, the Czech Republic, Estonia and Latvia are presented.

1.2.2. Measurement programmes

- in **Belgium** at iron ore sintering plants located in the Walloon region,
- in **Denmark** at a municipal waste incinerator msw with co-combustion of hospital wastes,

- in **Greece** at an electric arc furnace steel plant, a bio-waste (from olive production) drying installation and a hospital waste incinerator,
- in **Portugal** at hospital waste incinerators, an electric arc furnace steel plant and a secondary aluminium smelter
- in **Germany** at cold air cupola furnaces (iron/steal foundries), at various facilities suspected to emit dioxins and related compounds, at heavy duty diesel engines and regarding the problem of dioxin emissions from coal-fired domestic single room heating stoves.

1.3 Execution of the sub-projects

As agreed with DG Environment LUA NRW took over the obligation of negotiating with the partner institutes, co-ordinating the different measurement programmes and finally reporting. Moreover, in order to assure a good quality of the emission measurements LUA developed a standard scheme for the emission measurement reports and analysed one of the sampling extracts per each investigated facility in its own dioxin laboratory (cross-check analysis).

1.3.1. Measurement reports

Based on the EN 1948 standard for dioxin emission measurements a standard reporting form was programmed using the spreadsheet calculation program MS Excel®. Its application was generally required for all measurements done within this project. This spreadsheet program was designed to allow for using it directly at the site of measurement if feasible. It contains automated procedures to convert measured parameters (e. g. flue gas pressures) into those values needed for the consecutive steps of sampling (e.g. flue gas velocities for the selection of the best suited sampling probe diameter). Further, all measurement parameters which are to be reported according to EN 1948 and the standard ISO 9096 for emission sampling, are listed in the spreadsheets which are shown in ANNEX 1. The spreadsheet forms correspond to one particular sampling; hence, for a measurement campaign consisting of 3 samplings these forms had to be filled in 3 times, however, a number of information requested in these forms usually remains constant throughout a campaign thus reducing the necessary effort.

A further form was developed for the summarised reporting on the results obtained by several samplings at a particular facility. This form was a document file (MS word®) based on the standard measurement report (LAI-standard report[1]) required in Germany for all emission measurements which are carried out within the framework of governmental control activities.

The form developed for the dioxin project is reprinted in ANNEX 2. It requires quite a large amount of additional data (like composition of test gases used for calibration of measurement devices) which is assumed to be constant for a particular measurement campaign but might change over a longer period of time. It should be noted that the LAI standard report was developed to be applied for any type of emission measurement and thus it is much more comprehensive than the report form used within this project. The newly developed form contains only those parameters needed for dioxin emission measurements.

There were mainly two intentions why this way of reporting was chosen:

- With respect to the measurements carried out within Stage II it was anticipated that each laboratory involved would use its own unique report form having a different structure and therefore causing considerable search efforts if comparison of specific measurement data should be made. Such comparisons were thought to be a general need within the projects of Stage II. In a standardised sampling report one may find the same information always at the same place thus facilitating comparison between different samplings and/or different campaigns at similar emission sources.
- Up to now, there is no European standard measurement report available for PCDD/F emission measurements according to EN 1948. Comparable reports comprising all data needed to evaluate the quality of measurements thus cannot be expected if different laboratories working in different countries are committed to do the measurements. Even if the laboratories use methods agreeing with EN 1948 the reports could easily become incomplete because in the different parts of EN 1948 the parameters to be reported for a complete measurement are to some degree dispersed and thus cannot be extracted from the standard with ease. Further, those parameters generally needed to describe the state of flue gases are subjected of the reference standard ISO 9096 which must be consulted separately. Therefore, with the standard forms developed in this project it was intended to

---

[1] Ermittlung der Emissionen und Immissionen von luftverunreinigenden Stoffen, Geräuschen und Erschütterungen sowie der Prüfung technischer Geräte und Einrichtungen, Gem. Rd. Erl. d. Ministeriums für Umwelt, Raumordnung und Landwirtschaft vom 21.06.1996 -VA3-8817.4.2/8843.2 (V Nr. 6/91) und des Ministeriums für Wirtschaft, Mittelstand und Technologie -133-81-3.7 (12/91) - v. 06.01.1992, MBl NW. 1992 S. 314 (SMBL 7130)

assure completeness of reports and to gather first experiences on a European scale with such standardisation.

As a general result, all involved institutes accepted to report their data using the standard forms but none did apply it directly in the field. All institutes used their own common procedures for data acquisition. Data were transferred to the standard forms after the measurements and analysis had been completed. This of course increased the effort for the responsible people since they had to type all data twice and into different forms. However, this was in some cases advantageous since some errors could be detected by that way which still had remained in the spreadsheets in spite of extensive testing prior to their external application.

From a number of reports submitted it could be seen that EN 1948 could not be applied completely for the emission measurements. In most cases this was due to technical problems at the measuring site (bad accessibility of flue gas, large stack diameters hindering complete net measurements of flue gas velocities). In one case the analytical procedure deviated slightly from the method required by EN 1948. However, these limitations never were considered so severe that the measuring results had to be challenged. This view was supported by the fact that the cross check control samples analysed at LUA did agree in within acceptable ranges with the results of the external institutes.

Being the first attempt to put emission measurement reporting within an international project on a standard basis the applied procedure proved to be useful. However, for the future it is recommended to refine the report forms in connection with the revision of EN 1948 in order to remove unneeded parameters and to improve applicability.

1.3.2. Cross-check analyses

To have at least a minimum possibility of checking the emission measurement quality it was agreed with the partner institutes that one sample extract per each campaign (corresponding to one particular facility) should be analysed in parallel by the external institute and by the LUA dioxin laboratory. For this purpose, the sampling apparatus was extracted by the sampling team as usual with the exception that no extraction standard solution was added prior to extraction. The extract obtained then was reduced by evaporation to a defined volume. A well defined aliquot of this extract (generally 50%) was send to LUA for further analysis; the remaining aliquot was analysed by the external laboratory. Thus in the case of the cross-check analyses the extraction standard solution was added after extraction; moreover, each laboratory used its own extraction standards.

This procedure added the possible deviations between the used standard solutions as a further potential source of error. To deal with this problem in case of differing results, an aliquot of the extraction standard solution used by the external institute was also submitted. However, a comparison of the standard solutions did not become became necessary in any case as the results of the cross-check samples obtained by LUA and the external institutes were always in acceptable agreement.

2. Desktop study 1: Domestic solid fuel combustion

2.1. Proposal on research needed

2.1.1. Summary

In this sub-project the scope of a research program on dioxin emissions from domestic solid fuel (wood, coal) combustion was evaluated and a corresponding research proposal presented.

The proposal is aimed at heating facilities with central boilers (< 50 kW) and single stoves. Emission measurements should be carried out on-site in households and at test facilities in order to get data on special fuels. A minimum amount of 60 on-site samplings and 18 test-ring samplings was estimated to produce the data base needed for an improvement of the emission factors. Additionally the total cost of 385.000 EURO for a research project was estimated for the participating institutions/national authorities and the European Commission. A period of 18 months was estimated to be necessary for the entire project.

2.1.2. Background

In the Stage I report dioxin emissions from domestic combustion (for heating and cooking) were assessed to be potentially of high relevance for the annual European PCDD/F release. While the combustion of liquid and gaseous fuels was confirmed to be negligible, the use of solid fuels, e. g. wood and - less relevant - coal, was estimated to cause high emissions. However, this assessment was based on very uncertain basic assumptions concerning the quality of the burned material -in particular regarding different sorts of wood- and on the amount actually consumed in the European countries. A rough assignment of emission factors and of the consumed quantities of three material classes (clean, moderately polluted, highly polluted wood) revealed an annual emission estimate of nearly 1.000 g I-TEQ/a for the 17 countries considered in Stage 1, which however may be an overestimate. There are two aspects which affect the requirement to reduce the uncertainty of the emission estimate:

- Industrial dioxin emissions into the atmosphere are currently dominated by a few emission source types, particularly MSW incineration and iron ore sintering plants. After implementation of reduction measures at these sources the remaining industrial emissions will be generated from a large variety of facilities belonging to different industrial sectors. These remaining industrial emissions may occur at comparable or perhaps even minor emission levels than emissions from domestic burning. Any additional legal action aiming at abatement obligations would afford justification due to the fact, that any reduction achieved might be unimportant compared to the constant level of non-industrial emissions. The higher this level is, the more opposition is likely to arise against emission reduction requirements. Thus, future environmental policy measures on the industrial sector with respect to dioxin emission reduction might be linked directly to and limited by the assessed emission estimate for non-industrial sources.

- The second question arises from the constant „background“ level caused by the emissions from non industrial sources, which predominantly means domestic combustion. May this constant „background“ level be considered tolerable in view of the persistence of dioxins and furans and with respect to public health?

Recently, WHO changed the toxicity equivalent factors for PCDD/PCDF, reducing the tolerable daily intake (TDI) and increasing the number of compounds included into the calculation of the Toxicity Equivalent (TEQ). Together, all these measures result in a virtual aggravation of the situation regarding environmental pollution by persistent organic compounds (POPs). For example, before WHO’s reassessment the average daily intake of PCDD/Fs was nearly 1 pg I-TEQ/day*kg body weight. This was well below the old WHO TDI of 10 pg I-TEQ/day*kg body weight and approached the German target value. After the reassessment the margin between actual intake and TDI (now 1 - 4 pg I-TEQ/day*kg body weight) has decreased considerably; and with PCBs taken into account the daily intake would be somewhere in between the new WHO TDI range. Thus additional pressure is put on environmental authorities to further reduce the release of POPs into the environment.

It is likely that future toxicological research will present results which in turn will urge the WHO to go further steps into the direction of a lower TDI. It then will depend on the actual level of emission from domestic burning — which appears to be the only manageable non-industrial emission source type (besides the less relevant traffic emissions) — if a point is reached at which legal action with respect to this source of dioxin emissions may become inevitable.

2.1.3. Results and discussion

Since — as mentioned above — the uncertainty of the emission estimate is caused by uncertain emission factors for fuels used in Europe and by the lack of reliable statistical consumption data both factors must be improved at first to get more accurate annual emission estimates. However, right at the start of Stage II it soon became clear that a measurement program for the evaluation of reliable emission factors for different kinds of solid fuels used in different European countries would require the entire project fund being available at that time. In view of this, for practical reason and keeping in mind that abatement measures aiming at domestic burning are more likely to be a future task, this topic was separated from the others on the Stage II workshop in 1997. The participants from those countries which - due to the particularities of domestic heating in their countries – were most interested in this topic were asked to evaluate the scope of a related research program and to present a corresponding research proposal. A small part of the Stage II fund was spent on this „study“ which was elaborated by 4 institutions under leadership of the Austrian FTU. In the following, only the main features of this proposal [1] are summarised:

- The considered heating facilities comprise central boilers (< 50 kW) and single stoves.
- The emission measurements should be conducted either on-site (i.e. in households at the heating facilities installed therein) and at a test facility in order to get data on special fuels not covered by the on-site measurements.
- 60 on-site samplings and 18 test-ring samplings are expected to produce the minimum data base needed for an improvement of the emission factors.
- A total cost of 385.000 EURO was estimated which should be raised by the participating institutions/national authorities and by the European Commission both sides contributing 50% each.
- A period of 18 months, if the project starts in the summer season, was estimated to be necessary. (Remark: Due to the planned on-site measurements which can take place only during the heating period a shift of the starting point may lead to a prolongation of such a project.)

In order to ensure the necessary time for a decision the proposal was handed over to DG XI already in March 1999 together with a letter of recommendation [2].

Until the end of Stage II a considerable part of the work proposed in the FTU report was already carried out by LUA and the Austrian Umweltbundesamt. This regards the combustion of coal and coal-derived fuels in single room heating stoves. The investigations were made at test rigs and on site at a building chimney. Results are presented in this report (Vol 2, chapter 12). Thus, the main focus of the project as outlined in the FTU report can now be put onto domestic wood combustion.

References

1. C. Hübner, W. Moche, S. Manö, B. Rijpkema and A. Grochowalski, European Dioxin Project; Project Proposal PCDD/F Emissions from Domestic Combustion, p. 11. FTU GmbH (1999).
2. LUA, Communication to DG Environment.;, 1999.

3. Desktop study II

3.1. Dioxin Emissions to Land and Water

3.1.1. Summary

There are 5 sources comprising nearly 90 % of the total release of dioxins to land. The highly uncertain emissions from pesticide production (13.000 g I-TEQ (1994)) and use (1.600 g I-TEQ (1994)) will be decreasing because of improved control and reductions in the use of production of chlorinated pesticides and intermediates. Emissions from incineration of MSW of 7.200 g I-TEQ (1994) are decreasing because of improved combustion and control technology. The trends for the highly uncertain emissions from accidental fires 7.950 g I-TEQ (1994) and disposal of MSW to landfill 4.000 g I-TEQ (1994) are unpredictable. Other sources of dioxin releases to land are of less importance.

There are far less data available to enable releases to water to be estimated thus for most sources only an indication of whether the source is likely to release a high, medium or low emission to water is possible. The production and use of pesticides, chemical production, accidental fires (releases to water through fire fighting practices), disposal of MSW to landfill are deemed to be the highest potential sources for dioxin emissions to water.

3.1.2. Background

One of the major purposes of Stage II was to fill up the data gaps which had been identified in the Stage I report. Concerning emissions of PCCDD/F into land and water via production residues and/or products large uncertainties and only scarce data were found. Therefore a separate study on this topic was decided. A private technological consulting company, the AEA Technology plc, UK, was committed to do this work. The approach of this study was comparable to the approach of the report on air emissions in order to facilitate a synopsis of both results. By mid 1999 the final report on emissions to land and water was presented.

The entire report on dioxin emissions to land and water has already been published in the world wide web on the DG Environment home page (http://europa.eu.int/comm/environment/dioxin/); in the following, the final chapter (numbered “4”) of the AEA report is reprinted in order to give a brief survey on the results.

3.1.3. Conclusions and Recommendations

3.1.3.1. Releases to Land

The following table 1 shows the sources with a high potential for release to land. The 'best estimates' have generally been taken as the mid-point of the min-max estimates.

Source	Release to land (best estimate) g I-TEQ (1994)	% of Total Release	Uncertainty (High/ Medium/ Low)	Likely trends in release from 1994
Pesticide Production	13.000	34 %	High	↓
Accidental Fires	7.950	21 %	High	?
Incineration of MSW	7.200	19 %	Medium	↓
Disposal of MSW to Landfill	4.000	10 %	High	?
Pesticide Use	1.600	4,2 %	High	↓
Secondary Lead Production	1.200	3,2 %	Medium	?
Combustion of Wood - Domestic	650	1,7 %	High	?
Secondary Copper Production	390	1,0 %	Medium	?
Electric Furnace Steel Plant	350	0,9 %	Medium	?
Secondary Aluminium Production	310	0,8 %	Medium	?

table 1 dioxin and furan sources with a high potential for release to land

The releases from 3 of the 5 highest emitting sources are likely to be decreasing. Emissions from pesticide production and use will be decreasing because of improved control and reductions in the use of production of chlorinated pesticides and intermediates. Emissions from incineration of MSW are decreasing because of improved combustion and control technology.

The estimated releases from 4 of the 5 highest emitting sources have a high uncertainty. There is a particularly high uncertainty regarding the estimated releases from accidental fires and from the disposal of MSW to landfill. The estimated releases to land as a result of accidental fires range from 3 to 15.900 g I-TEQ. This demonstrates the very high uncertainty in this release.

Releases to land from non-ferrous metal processes greatly depend on the proportion of dust from gas-cleaning technology that is recycled into the process instead of being disposed to land.

The disposal of sewage sludge to land has an estimated total release of PCDD/F of 180 g I-TEQ. It is a significant source for which releases to land have the potential to increase, because of improvements in waste water treatment and reduction in sewage sludge disposal to sea. Releases are likely to continue to be much lower than those from most of the sources in the above table, but sludge disposal presents a significant route for PCDD/Fs to enter food chains.

3.1.3.1.1. Recommendations

- The results indicate that the highest release to land is from pesticide production and that this source should be the highest priority for further work to improve the whole inventory.
- To improve the inventory of PCDD/F releases to land it is not just measurements of concentrations that are required. Further research is needed on details of activity and processes – this should involve contacting the industry trade associations and other relevant organisations in individual countries. For example, work to investigate the details of the extent of recycling of dusts at non-ferrous metal plant in different countries would greatly improve the reliability of these estimated releases.

3.1.3.2. Releases to Water

There are far less data available to enable releases to water to be estimated and for most sources an indication of whether the source is likely to release a high, medium or low emission to water has been given, rather than an estimate of the release quantified (see table 2).

Source	Potential release to land (min. – max.) g I-TEQ (1994)	Likely trends in release from 1994	Additional notes
Pesticide Production	High (no data)	↓	
Chemical Production	High (no data)	↓	Estimated release from PVC processes in Germany 0,15-51 g I-TEQ
Accidental Fires	High (no data)	?	
Disposal of MSW to Landfill	High (no data)	?	
Pesticide Use	High (no data)	↓	
Paper & Pulp Production	Medium (8 – 27)	↓	
Incineration	Medium (0,3 – 16)	↓	Estimated release for industrial waste incineration only
Waste oil disposal	Medium (1,8 – 7,9)	?	
Textile treatment	Medium (no data)	?	
Non-ferrous metal production	Medium (no data)	?	
Iron & steel industry	Medium (no data)	?	
Sinter plant	Medium (no data)	?	
Waste water treatment	Low (no data)	↓	

table 2 estimation of likelihood of dioxin and furan releases to water from certain sources

Whereas the release to land from accidental fires is difficult to control, there is potential for control of releases to water which occur through fire fighting practices.

As mentioned, the releases from pesticide and chemical production and use are likely to be decreasing because of the reduction in chlorinated chemical use. Releases from paper and pulp production have decreased with the phase out in chlorine bleaching. Releases from industrial processes (e.g. metals) will depend on the extent of use of scrubbers and the quality of effluent treatment. As with the treatment of municipal waste water, the PCDD/Fs from industrial waste waters are likely to concentrate in the sludge.

3.1.3.2.1. Recommendations

- As much of the PCDD/F contamination in waste waters is likely to be removed at treatment plant, and the PCDD/Fs therefore concentrate in the sludge, further work should focus on investigating the extent of waste water treatment and then on the concentration of PCDD/Fs in sludge as well as the sludge disposal practices.
- However, releases to water from chemical and pesticide production and use, from accidental fires and from MSW disposal to landfill, should be researched further through appropriate measurements and identification of more reliable activity data.

3.1.3.3. Uncertainty

There are very limited quantities of data available relating to PCDD/F releases to land and water and the estimates in this inventory are therefore very uncertain. For all the estimated releases there are significant uncertainties with one or more of the following :

- the activity / production data;
- the quantity of solid or liquid waste arising;
- the extent of control of releases;
- the concentration of PCDD/Fs in solid and liquid wastes.

These uncertainties are demonstrated by the very wide ranges in estimated emissions for sources where sufficient data were available to make estimates.

There is a particular lack of information on releases to water and, therefore, few quantitative estimates have been made for this medium.

However, this inventory of releases of PCDD/F to land and water, together with the inventory of releases of PCDD/F to air [1], is the first integrated inventory for releases of any POP in Europe. It represents a good starting point for improvement of the inventory and ultimately for appropriate development of future policy to further reduce or control releases of PCDD/Fs into the environment.

3.1.3.3.1. Recommendation

- As the inventory of releases to land and water is too uncertain to act as a reliable indicator in the development of further appropriate policy for emission reduction and control, it is recommended that further research and data collection are carried out to verify the scale of releases from the source sectors which have a high potential for release. These sectors are:
  - Chemical production and use
  - Pesticide production and use
  - Accidental fires
  - Disposal of MSW to landfill
  - Non-ferrous metal industry

3.1.3.4. General Conclusions and Recommendations

Estimated releases to land from known sources for which estimates have been made are significantly higher than releases to air, as shown below (see table 3):

	Release (g I-TEQ)		
	Min.	Max.	Best estimate
Land	3.850	72.600	38.200
Air [1]	1.320	20.000	3.270

[1] LUA 1997

table 3 estimated releases to land from known sources

While not quantified, total releases to water are likely to be significantly less than both releases to land and to air. This is because waste water treatment is likely to concentrate the PCDD/Fs in sludge. However, the extent of waste water treatment is likely to vary between sectors and between countries. Reduction of releases to water is still important as this is a key exposure route.

This default inventory for PCDD/F releases to land and water in 1994 has been built up from the main information sources on releases to land and water. At this stage it is mainly based on information which has been assembled for previous studies for the UK, Germany, Sweden and The Netherlands. Though this study has identified the majority of relevant published reports on releases of PCDD/Fs, there is likely to be much measurement data that has not been published.

The draft of this report was distributed to various international experts on PCDD/F emissions within the countries covered by the study. These experts checked the inventory and provided country-specific information where available. The draft inventory has therefore been improved since it was distributed in March 1999.

Some of the uncertainty in the inventory relates to the likelihood that techniques to measure PCDD/F concentrations do not always give comparable results.

3.1.3.4.1. Recommendations

- Further work to improve the inventory should concentrate on a balance between sources with a high potential emission (e.g. pesticide production, MSW incineration) and sources which are important in terms of environmental impact/exposure (e.g. pesticide use, sludge disposal).

- Despite the likelihood of releases to water being less than to land and air, this release route represents a key exposure route and improvements to the inventory are required so that the scale of releases can be assessed in different countries.
- It is recommended that the EU encourages the measurement and reporting of PCDD/F releases to the environment so that the inventory can be updated with more reliable data.
- As the integrated inventory is improved, it is important that the network of experts around Europe is maintained so that new information is taken into account. The large existing network within the UNECE Task Force on Emission Inventories provides an excellent base for raising awareness of new data.

The EU is also encouraged to continue the standardisation of sampling and analytical techniques. This will improve the comparability of data.

References

1. U. Quaß, M. Fermann and G. Bröker, Identification of Relevant Industrial Sources of Dioxins and Furans in Europe, LUA Materialien Nr. 43, 936 pp., Landesumweltamt NRW (1997).

4. France

4.1. The French Dioxin Emission Inventory

4.1.1. Summary

The French ministry of environment had decided to set up a fund for a separate comprehensive emission testing program, therefore, no contract was made with the French institution ADEME within this project. Nevertheless, it was agreed that data gathered within the French measurement program shall be reported in the framework of the European Dioxin Project as well.

For MSW incineration ADEME had estimated an annual emissions of around 400 g I-TEQ/year from the arithmetic mean of the emission factors. Using the published concentrations and multiplying them with a typical specific flue gas volume of 5000 m^3/ton waste and with a yearly operation time of 8000 hours the annual emissions obtained are: 435 g I-TEQ/year for 1997, 350 g I-TEQ/year for 1998 and 227 g I-TEQ/year for 1999. Abatement measures as well as closures of plants have reduced the emissions from MSW incinerators in France considerably and the actual situation in 2000 is likely to improve further. For the year 2000, annual emissions are assessed to be around 200 g I-TEQ/year. It appears unlikely that all existing plants will be retrofitted until 2005 to comply with the emission limit value of 0,1 ng I-TEQ/m^3, but in case the trend observed during the recent years will continue a further emission reduction by 50% seems to be realistic.

The results of the measurements carried out at iron ore sintering plants and secondary non-ferrous metal producing facilities within the French dioxin program were published in terms of annual emission freights only. These values can be converted to emission concentrations if the specific production values of the investigated plants are known. For the six French sintering plants emissions of 93 g I-TEQ/year are reported by the French dioxin survey. Thus, as in other countries with integrated steel works the French iron ore sintering process constitutes a considerable emission source too.

A number of electric arc steel works revealed to be rather strong dioxin emitting sources as well. Overall, 36 g I-TEQ/year were calculated mainly from the measurement results of 6 plants. Another 11,5 g I-TEQ were assigned to secondary aluminium production, whereas copper and lead production facilities were estimated to cause emissions of little more than 2 g

I-TEQ/year each. Slightly higher emissions of 3,4 g I-TEQ/year coming from iron foundries; coke ovens and some other installations in the metallurgical industries appeared to be of minor importance. One particular facility of the non-ferrous metal sector revealed to be by far the most relevant single source, it was estimated to emit about 200 g I-TEQ/year. According to the company a three step abatement program was carried out to reduce the emissions to less than 1 ng I-TEQ/m³. Measurements confirmed an emission reduction by more than 90%

Regarding other emission sources a considerable lack of knowledge still exists with respect to clinical waste incineration. There are 3 incinerators especially designed for hospital waste incineration. These installations presumably apply a pyrolysis reactor combined with a post-combustion unit. Additionally, one plant for hazardous waste incineration is mentioned. About 20 plants for municipal solid waste incineration are used for co-combustion of hospital waste. Besides these plants also on-site combustion facilities may still be in operation. The number of these small facilities was decreasing considerably during the last decade from about 1400 installations in 1991 to about 400 after 1994. How many on-site facilities actually are operated seems to be uncertain. No data were published yet on the distribution of hospital waste to the different types of plants and on measurement results from on-site incinerators. Dioxin emissions from co-incinerated hospital waste were already considered within the estimate for MSW incinerators. For 1995 a revised dioxin emission level between 10 and 50 g I-TEQ/year was estimated, the value form the lower end of this range being more probable due to continuing closures of small on-site incinerators and abatement measures at the co-incineration plants.

4.1.2. Background

In the Stage I report a preliminary dioxin emission inventory for France was presented which had been set up by the French agency ADEME [1]. This preliminary inventory was based on a few measurement results at municipal solid waste incinerators and on estimates relying on emission factors gathered from other countries for all other industries. The ADEME inventory revealed an urgent need for more information; hence, there was considerable interest in France to participate in Stage II of the European project.

However, at that point (by the end of 1997) the French ministry of environment decided to comply with the recommendations of ADEME and to set up a fund for a comprehensive emission testing program. Consequently, no contract could be made with ADEME within the

DG XI project. Nevertheless, ADEME agreed that data gathered within the French measurement program shall be reported in the framework of the European Dioxin Project as well.

The results of the emission measurements in France have been made available to the public on the internet site of the ministry of environment [2]. This site contains data on large MSW incinerators (> 6 tons waste per hour overall capacity) and facilities in the metal industry

4.1.3. Results and discussion

In the following, some explanations and comments on the results will be presented; an updated inventory for France can be found in Volume 3 of this report.

4.1.3.1. MSW incineration:

In the Stage I report an emission freight of ca. 160 g I-TEQ/year was calculated from the geometrically averaged emission factors which had been presented in the preliminary dioxin inventory. By contrast, ADEME estimated the annual emissions to be around 400 g I-TEQ/year from the arithmetic mean of the emission factors.

Looking at the measurement values published meanwhile ADEME’s view appears to be the more realistic assessment. Using the published concentrations and multiplying them with a typical specific flue gas volume of 5000 m³/ton waste and with a yearly operation time of 8.000 hours the following annual emissions are obtained for the years 1997, 1998 and 1999 (see table 1):

Year	**1997**	**1998**	**1999**
g I-TEQ/year	435	350	227

table 1 annual dioxin and furan emissions in France

For this calculation, the following further assumption were made in view of the different data available:

Case 1: Measurement results are available for all years

- If trend is decreasing, values were used as presented
- If values are fluctuating, the average concentration was used for all years.

Case 2: Results missing for 1997:

- If decreasing from 1998 to 1999 then the 1998 value was chosen for 1997, too; else an average value was assumed for 1997

Case 3: Results missing for 1998 and/or 1999:

- Depending on the trend, the last available results prescribed or the averages of presented were values used.

Based on these results, in the revised inventory for 1995 the emission calculated for 1997 is used. Clearly, abatement measures as well as closures of plants have reduced the emissions from MSW incinerators in France considerably. The actual situation in 2000 is likely to improve further (indicated closures of some plants by end of 1999 will save about 10 g I-TEQ/year). Hence, for the year 2000, annual emissions are assessed to be around 200 g I-TEQ/year.

Regarding the near future it appears unlikely that all existing plants will be retrofitted until 2005 to comply with the emission limit of 0,1 ng I-TEQ/m^3. In case the trend observed during the recent years will continue a further emission reduction by 50% seems to be realistic.

4.1.3.2. Metal industry:

From experiences made during the assessments of dioxin emission in other countries it was known that metallurgical plants may have considerable impact on the annual dioxin release. In particular, iron ore sintering plants and secondary non-ferrous metal producing facilities are of concern. Thus, a number of measurements were carried out at such emission sources within the french dioxin program. The results were published in terms of annual emission freights only. These values can be converted to emission concentrations if the specific production values of the investigated plants are known.

Regarding iron ore sintering, annual dioxin emissions of 128 g I-TEQ/year were estimated for the six French plants in the Stage I report based on the 1994 production and an emission factor of 7 µg I-TEQ/ton sinter. Actually, slightly lower emissions (93 g I-TEQ/year) are reported by the French dioxin survey. Fortunately, the more pessimistic assessment of the preliminary dioxin inventory which contained a range of estimation from 220 to 2.200 g I-TEQ/year was not confirmed. Nevertheless, as in other countries with integrated steel works too the French iron ore sintering process constitutes a considerable emission source.

Besides sintering plants also a number of electric arc steel works revealed to be rather strong dioxin emitting sources. Overall, an annual emission of 36 g I-TEQ/year was calculated from the measurement results, generated mainly by 6 plants which contribute about 33 g I-TEQ/year. Another 11,5 g I-TEQ were assigned to secondary aluminium production, whereas copper and lead production facilities were estimated to cause emissions of little more than 2 g I-TEQ/year each. Slightly higher emissions of 3,4 g I-TEQ/year coming from iron foundries; cokeries and some other installations in the metallurgical industries appeared to be of minor importance.

However, it was a surprise to the French public that one particular facility of the non-ferrous metal sector revealed to be by far the most relevant single source. The Recytech plant, a sister company of the German BUS — of which PCDD/F emissions also have been of major concern in Germany — was estimated to emit about 200 g I-TEQ/year. A sketch of the production process of this plant which recovers zinc from residual materials like filter dusts from metallurgical industries is shown in figure 1.

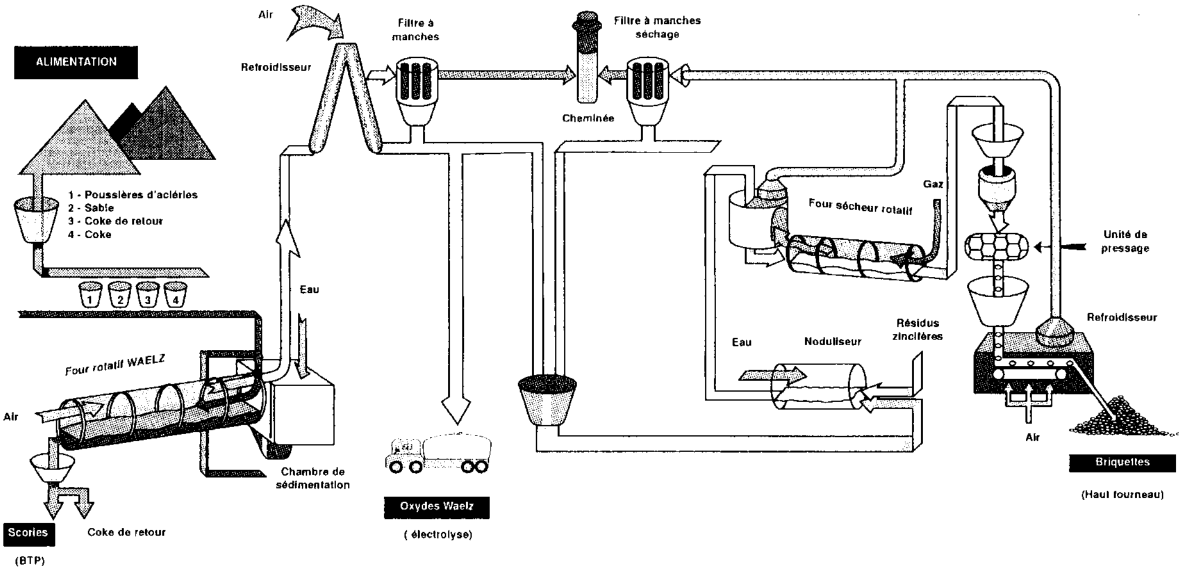

figure 1 Sketch of the zinc recovering plant

Apparently, when the first measurements were carried out the only flue gas cleaning system installed consisted of a fabric filter within each waste gas duct before entering the stack.

According to the company and since these high emission data became public, a three step abatement program has been carried out (see figure 2) comprising of:

1. rapid cooling of the flue gas leaving the waelz furnace,
2. installing of a coke injection in connection with a contact reactor and an additional fabric filter,
3. separation of waste gases generated by the rotary drum used for drying (20.000 m³/h) and by the briquette cooling unit (50.000 m³/h), respectively. Cleaning of the flue gas from the rotary drum is achieved by an additional fabric filter and a fixed-bed lignite absorber, while the larger volume of the cooler flue gas still passes the fabric filter which already existed.

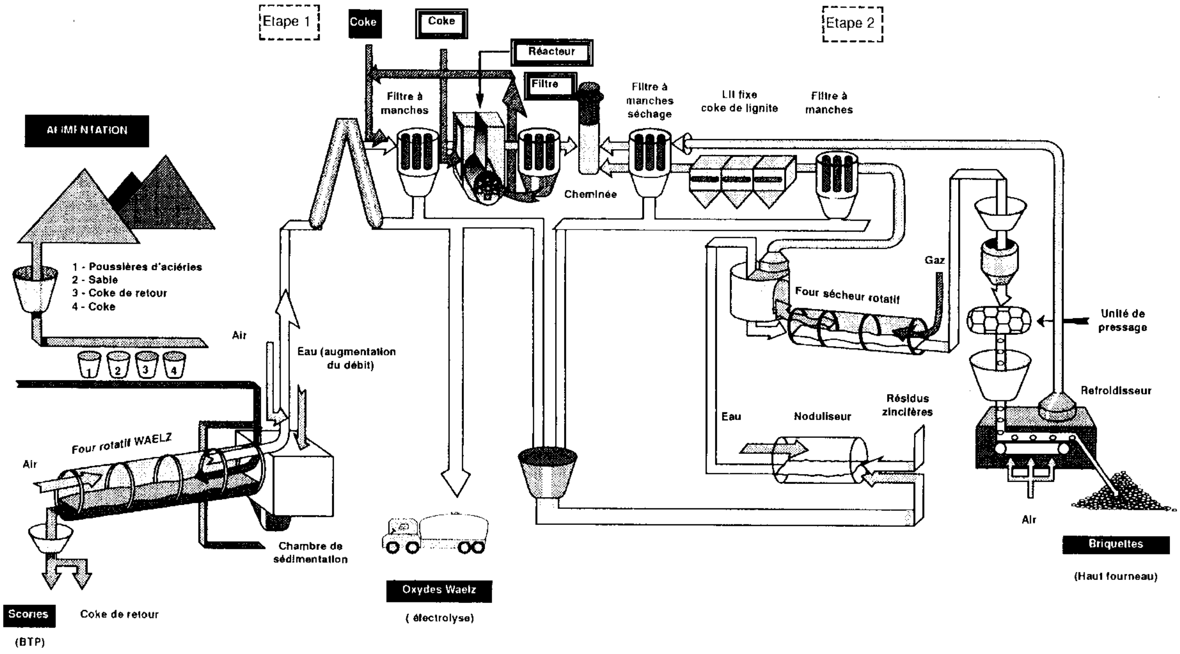

figure 2 Sketch of the zinc recovering plant after the three step abatement program

It was anticipated that the PCDD/F concentrations in the flue gas would decrease from 130 ng I-TEQ/m^3 to less than 1 ng I-TEQ/m^3. By mid of June 1999, having finished the second of three abatement steps, measurements showed concentrations between 1 and 5 ng I-TEQ/m³, thus confirming an emission reduction by more than 90% (see figure 3).

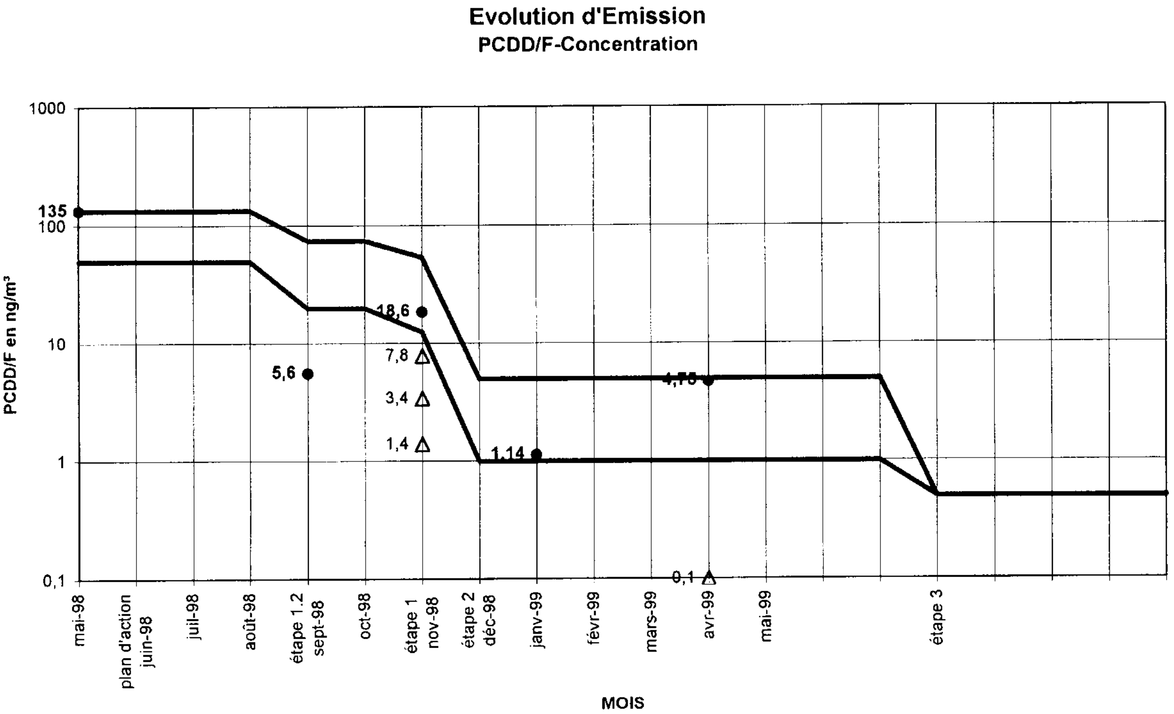

figure 3 Reduction of dioxin emissions by introduction of the three step abatement program

The case of the Recytech plant demonstrates that emission measurements at all facilities which are suspected to be a dioxin source are inevitable to get a true picture of the emission situation.

4.1.3.3. Other sectors

Regarding other industrial emission sources a considerable lack of knowledge still exists with respect to clinical waste incineration. From information found in the internet [3] the general situation of hospital waste incineration in France appears to be as follows:

- There are few (almost 3) incinerators in operation specially designed for hospital waste incineration. These installations presumably apply a pyrolysis reactor combined with a post-combustion unit. Additionally, one plant for hazardous waste incineration is mentioned.

- A number of plants (about 20) for municipal solid waste incineration are used for co-incineration of hospital waste. According to the French regulation the fraction of hospital waste may not exceed 10%.
- Besides the plants mentioned above also on-site combustion facilities may still be in operation. The number of these small facilities is said to be decreasing considerably during the last decade. For example, in 1991 in ca. 2600 “établissements de soins” about 1400 installations were operated. By 1994, more than 1000 were on the way to closure. However, even by 1996 hospital waste incinerators had not been included explicitly in the regulative system of administrative authorisation. Actually it seems to be uncertain how many on-site facilities are operated.

Regarding the overall dioxin emissions from this sector it can be stated, that emissions caused by hospital waste being co-incinerated with municipal waste are already considered within the estimate for msw incinerators. Therefore, it may be concluded that the emission value for hospital waste incineration presumably was an overestimate. No statistical data on the distribution of hospital waste to the different types of plants could be obtained, and, furthermore, no measurement results from on-site incinerators have been published yet. Hence, for the revised 1995 dioxin estimation a range of 10 up to 50 g I-TEQ/year is chosen. Regarding the actual situation it is assumed that a value form the lower end of this range is more probable due to continuing closures of small on-site incinerators and abatement measures at the co-incineration plants. Based on the presumption that this trend continues in the near future for the year 2001 an emission of 1 g I-TEQ/year may be possible.

4.1.4. Conclusion

Summarising the dioxin emission situation in France it can be characterised by emissions originating from large msw incineration plants and metallurgical industries of about 850 g I-TEQ/year at the time the measurement program was started. According to a recent evaluation presented on the environmental ministry’s homepage [4] in the meantime, this emission freight has been lowered considerably to about 340 g I-TEQ/year. This was achieved by closing or upgrading of msw incinerators as well as the by emission reduction at the recytech zinc recovery plant. However, measurement data or emission freights obtained at small incinerators still have not been published; it should therefore be kept in mind that at the time being the actual emissions may be somewhat higher. Nevertheless, assuming compliance to the 0,1 ng I-TEQ/m³ limit value of the designated European Directive on Waste incineration further reduction by 190 g I-TEQ/a can be projected.

Besides the sectors mentioned the French Ministry of Environment is aware of further emission sources which however have not yet been investigated in detail. These sources comprise cable reclamation (4.000 tons per year) which may give emissions of 40 g I-TEQ/a and industrial wood combustion (including waste wood) adding ca. 15 g I-TEQ/a. Domestic wood combustion is estimated to contribute between 30 and 100 g per year depending on the amount of polluted wood being burned.

References

1. A. Milhaut and H. Pernin, Preliminary Dioxin Emission Inventory in France, 6 pp., ADEME (1996).
2. Ministère du l'Aménagement du territoire et de l'Environnement: http://www.environnement.gouv.fr/actua/cominfos/dosdir/DIRPPR/dioxine/tabdioxines.htm#s.
3. l'Association de Cadres de SANté (A.C.SAN): http://www.multimania.com/ca1998/LAGESTIONWEBDESDECHETSHOSPITALIERS.htm.
4. Ministère du l'Aménagement du territoire et de l'Environnement: http://www.environnement.gouv.fr/actua/cominfos/dosdir/DIRPPR/dioxine/2k0706-evol-emission-dioxine.htm).

5. Dioxin emission data from Central European Countries

5.1. Summary

This chapter comprises an overview on information available from four Central European countries: Poland, Czech Republic, Estonia and Latvia. This information has been gathered either within an intense communication between LUA and relevant authorities or experts in these countries or from international publications.

In case of Poland, the main emphasis is put on hospital waste incinerators. About 45 % (ca. 85.000 t/year) from the total annual amount of hospital waste in Poland (about 187.000 t in 1997) is disposed off in landfills. The remaining 103.000 t/year are incinerated in power plants, local hospital heating facilities and waste incinerators. Around 75.000 t/year are incinerated in about 300 old obsolete incinerators build between 1960 and 1980. The 300 old incinerators contribute at an average of 15 ng I-TEQ/m3 to the total atmospheric dioxin pollution in Poland. The 25 modern hospital waste incinerators emitted about 0,08 ng I-TEQ/m^3 of dioxins if huge, fresh carbon filters were used. Just before replacing of used-up carbon filters the dioxin concentrations increased up to 25 ng/m^3.

A special question was tried to answer in case of the co-operation with Estonia. The Estonian thermal power station near Narva is the world largest thermal power station burning low-grade local oil shale. In preparation of a measuring campaign filter ash and raw oil shale dust samples were analysed first. If dioxins are formed during the combustion of oil shale they should be found in filter ash samples of the plant concerned. The PCDD/F concentrations obtained were near the lower end of the range covered by PCDD/F filter dust contents analysed in samples from German hard coal and brown coal combustion plants (0,3 - 21 ng I-TEQ/kg). The found filter dust concentrations correspond with flue gas concentrations of well below 0,1 ng I-TEQ/m^3. Therefore the results obtained for the oil shale samples neither did indicate a considerable input of polychlorinated organic compounds nor their formation and emission during the combustion process. Based on the results obtained it was unlikely that the oil shale combustion plant in Estonia is a relevant emission source for dioxins and furans.

From Latvia only a compilation of industrial activities which presumably may cause dioxin emissions to air was received. These include some potentially relevant sources:

- municipal and hospital waste incinerators and

- (illegal) non-ferrous scrap processing installations.

Unfortunately, no measurements of handled materials or emissions could be carried out.

In the Czech Republic comprehensive investigations took place in the recent years which led to the establishment of an emission inventory. Data are presented for the period 1990 to 1998 showing a steady decrease of emissions from 2.200 g I-TEQ/a down to 1.380 g I-TEQ/year, respectively. Another study [1], at least partly using the same measurement data, reports different estimates with 1990 emissions of 1.252 g I-TEQ/a and a decrease down to 770 g I-TEQ/a in 1998. Most relevant sources in both inventories are iron ore sinter plants (> 70 g I-TEQ/a in 1998) and domestic burning (ca. 390 g I-TEQ/a)

5.1.1. Background

With respect to the wishes of East- and Middle European countries to become members of the European Community DG XI requested to include some of these countries into the European Dioxin Project. Hence, LUA looked for contacts in the Baltic countries and in Poland inviting to participate and asking for proposals. Except for Lithuania responses were received from the other three countries and delegates attended the project workshop in Essen, November 1997.

Only the participant from Poland was able to propose an emission measurement program. He highlighted to investigate the liability of clinical waste incineration for dioxin emissions in Poland and suggested to carry out measurements at some facilities in order to evaluate the reliability of results already available.

The other two countries Estonia and Latvia do not have any laboratory experience in sampling and analysis of dioxins. Yet Estonia appears to have the most developed environmental policy of the Baltic countries; but in general, emission control — where required — is done by companies located in Finland.

In Estonia neither waste incineration plants nor plants of the metallurgical industry are operated. As these types of plants are the most important dioxin sources in West Europe it was assumed that dioxins are emitted to a lower extent only. However, in Estonia oil shale combustion plants for power generation are operated; they are the largest combustion plants in that country and must be considered unique. No information was available so far about possible dioxin emissions from plants burning this kind of fuel.

During the Stage II start-up workshop it was decided to install a Polish sub-project comprising measurements at selected clinical waste incinerators; however, since a lot of information revealed to be already available emission measurements were unnecessary and thus the sub-project finally was changed into a voluntary co-operation. LUA further took over the obligation of carrying out laboratory measurements to evaluate the likelihood of dioxin emissions from oil shale combustion and to stay in contact with the Latvian authorities in order to collect information about possible emission sources.

Moreover, during the last year of Stage II some relevant information on dioxin emissions in the Czech Republic became available. As this country also belongs to the EU accession countries this information is also reviewed here.

5.1.2. Results and discussion

5.1.2.1. Hospital waste incineration in Poland

In accordance with the relevance list of emission sources agreed on the project workshop hospital waste incineration was considered as one of the most important sources. This assessment was based on the results of Stage I which stated that:

- the emission factors observed at hospital waste incinerators cover a wide range
- the statistical data on hospital waste incineration are limited and somehow inconsistent

The preliminary information provided by the Polish partner institute and based on own surveillance revealed that considering dioxin emissions in Poland hospital waste incinerators are of significant interest. The following table 1 gives a summarised overview on the treatment of hospital wastes in Poland:

treatment of hospital wastes	amount in tons/year
deposition on municipal dumps (total) (infectious waste)	80.000 4.800
incineration in power plants or local hospital heating facilities	22.000
incineration in old obsolete plants (about 300 plants) *	75.000
incineration in modern plants (25 plants)	10.000 **
incineration in newly constructed small incinerators (20 plants)	(estimated) 200-500
waste buried in graves	≤ 20
total hospital waste in 1997	About 187.000

table 1 hospital waste treatment in Poland in 1997

*** Mostly installed between 1960 and 1980 (one plant from 1930!)**
**** Estimated value because many of these plants operate in less than nominal capacity**

The average capacities of the 300 old hospital waste incinerators are normally between 50 to 100 kg/h of hospital wastes. This is only an approximation of the capacity because even if an old incinerator was originally designated for a capacity of 100 kg/h it may be operated with 30 kg/h as well 150 kg/h of waste. There are also some incinerators having higher capacities than 300 kg/h, but they are not dominant.

The old hospital waste incinerator are mostly oil or gas heated chamber furnaces equipped only with a cyclone as waste gas cleaning device. Due to upgrading of old incinerators it is difficult do establish how many of them are operated with this kind of furnace, this may apply to about 80 % of the old incinerators. About 30 old incinerators are equipped with low efficient spray absorbers using aqueous alkali solutions.

The incineration of hospital waste is generally under control of insufficiently qualified personnel. Thus there is no control of waste materials fed into the incinerators and the waste material is not separated before incineration. Therefore wastes from households, mechanical department (oily wastes) and some municipal wastes are found mix up with hospital wastes though of course mainly hospital wastes are burned. It is very difficult to asses the ratio of hospital wastes versus the other wastes because it depends on the actual waste treatment policy of each hospital.

The average dioxin emission from these incinerators was estimated to lie on a level of 10 to 20 ng I-TEQ/m^3. In singular cases higher emission may occur e.g. 32 ng I-TEQ/m^3 were found at one plant.

Yet, available measurement data are sufficient to estimate the average flue gas concentration of the 300 old incinerators which leads to a contribution at an average of 15 ng I-TEQ/m^3 [2].

The average capacities of the 25 modern hospital waste incinerators are normally between 50 to 1200 kg/h of hospital wastes. These plants are mostly pyrolytic incinerators with dry and/or wet stack gas cleaning except for one plant being a rotary kiln with a dry and wet gas cleaning device (table 2).

type of incinerator	stack gas cleaning	number
pyrolytic	only dry	3
pyrolytic	dry and wet	6
pyrolytic	only wet	15
rotary kiln	dry and wet	1

table 2 overview on modern hospital waste incinerators in Poland

The plants with dry stack gas cleaning only are equipped with a pyrolytic chamber operated at 600 to 800 °C. The gases of the pyrolysis are directed to an afterburner operated at 1100 °C and afterwards to a heat exchanger were they are cooled down to 250 to 300 °C. Finally, the stack gases pass an activated carbon filter and/or a bed of dry granulated calcium hydroxide. When huge, fresh carbon filters were used dioxin concentrations of about 0,08 ng/m³ were found. Just before replacing of used-up carbon filters the dioxin concentrations increased up to 25 ng/m³. The dioxin concentration in saturated active carbon was about 50 µg I-TEQ/kg.

The installations with dry and wet stack gas cleaning use in practice the same technology as the above mentioned plants. They are equipped with a pyrolytic chamber operated at 500 to 800 °C, a thermo reactor operated at 1100 to 1200 °C and a high efficiency heat exchanger which cools down the gases to 300 °C. The stack gases pass through a water quench (temperature up to 150 °C), a sorbent spray (sorbalit), a baghouse filter and an alkali water two stage absorbing tower. The water of the absorbing tower is reused for the water quench, therefore no waste water must be drain off, however problems occur with the deposition of used sorbalit and ash from the pyrolytic chamber. Dioxin levels were found between 0,02 and 0,06 ng/m³.

The plants with wet stack gas cleaning only are equipped with a pyrolytic chamber operated at 600 to 800 °C, a thermo reactor with supplemental air feeding and a heat exchanger which cools the stack gases down to about 300 °C. Finally the stack gases are lead through an alkali scrubber system with or without quench for cleaning. The found dioxin concentrations for this type of installation lied between 0,2 and 3,5 ng/m³.

The rotary kiln with dry and wet stack gas cleaning is operated at about 600 °C (sometimes up to 850 °C). The normal capacity is 200 kg/h though occasionally it is operated with 500 kg/h. The stack gases pass through a cyclone, a not very effective baghouse filter and an absorbing tower filled with an alkaline aqueous solution (produces about 1 m³/h of waster water). The dioxin level at this plant was found to be about 2 to 5 ng/m³. The following table 3 gives an overview on all measuring results from the modern hospital waste incinerators.

type of incinerator	stack gas cleaning	ng I-TEQ/m³*
pyrolytic	only dry	0,08
pyrolytic	dry and wet	0,02 - 0,06
pyrolytic	only wet	0,2 - 3,5
rotary kiln	dry and wet	2 - 5

table 3 dioxin emission factors form modern hospital waste incinerators in Poland

*** all dioxin concentrations for dry gas, 11 % O2, 0,1 MPa and 273 K**

The data from 13 of the new incinerators — some of them were investigated several times — did not prove any significant influence on atmospheric dioxin concentrations. Therefore according to the Polish informant it was not necessary to do measuring campaigns at these facilities.

Some amount of hospital wastes is co-incinerated in power plants. In 1997 a new law was enacted in Poland concerning treatment of hazardous waste. However, it remains questionable if the implementation of this new law is effective yet. So, it may be expected that the amount of hospital wastes incinerated in power plants,–is still valid. The considered power plants are rather small they mainly serve for local, hospital needs. The wastes packed in plastic bags are not shredded, milled, sieved or treated in any way before incineration. They are fed in their original form into the grate furnaces. These grate furnaces and boilers are still operated in many hospitals as a local steam source. Measuring dioxins at these facilities is not difficult but the results depend on the used fuel. On some days the fuel is mixed up with wastes, on other days not, and this may change daily.

5.1.2.2. Oil shale combustion in Estonia

The preliminary information provided by the Estonian informant revealed that considering dioxin emissions in Estonia a thermal power station firing oil shale might be of interest.

This Estonian thermal power station is the world largest thermal power station burning low-grade local shale. The station is situated near the city of Narva, it is incorporated in the Estonian Power System. The specific properties of the local shale, such as its low calorific power (2000 kcal/kg), high ash content (43,6 %) and moisture (12 %), formation of thick ash deposits on the heating surfaces of boilers and abrasive property of the ash had set a number of engineering problems (table 4).

capacity	1600 MW
fuel consumption per hour	244 t/h
fuel consumption per year	12×10^6 t
sulphur content of fuel	1,5 - 1,6 %
amount of stack gas per kg fuel	3,97 nm³/kg
concentration of ash in stack gas	1220 mg/m³
concentration of SO_2	1500 mg/m³
concentration of NO_x	206 mg/m³

table 4 Technical data of the oil shale power station

As no date were available about possible dioxin emissions from oil shale combustion plants a measuring campaign was considered. In preparation of the measurements the Estonian informant was asked for filter ash and raw oil shale dust samples. If dioxins are formed during the combustion of oil shale they should be found in filter ash samples of the plant concerned.

The analyses of the samples from the Estonian oil shale combustion plant were carried out in the laboratories of LUA. The samples were analysed with high resolution GC/MS methods for their content of polychlorinated biphenyls (PCB), polychlorinated dibenzo-p-dioxins and dibenzofurans (PCDD/F) and with a semi-quantitative x-ray fluorescence procedure for chlorine and a number of inorganic compounds.

Moreover, the ignition loss (by heating of the samples to 800 °C for 3 hours) was determined. Mass losses were found to be 43,4 % ("oil shale ash") and 2,3 % ("oil shale dust"), respectively. Apparently, more material was combusted in the filter ash than in the unburned raw oil shale dust. From this results it can be assumed that the designation of the samples — which looked very similar — was incorrect and that it was mixed up prior to shipping them to LUA

However, the assumed exchange of the samples did not matter since the PCB and PCDD/F contents of both samples were very low, with a number of congeners being below the analytical detection limits. The PCB concentrations were higher in the "ash" sample with overall levels being comparable to those usually found in blank or background samples (sum of tri- to decachlorobiphenyls around 2 µg/kg).

The PCDD/F contents were slightly more concentrated in the "dust" sample. The PCDD/F concentrations obtained were near the lower end of the range covered by PCDD/F filter dust contents analysed in samples from German hard coal and brown coal combustion plants (0,3 - 21 ng I-TEQ/kg).

The found filter dust concentrations are likely to correspond with flue gas concentrations of well below 0,1 ng I-TEQ/m³. Therefore the results obtained for the oil shale samples neither did indicate a considerable input of polychlorinated organic compounds nor their formation and emission during the combustion process.

Based on the results obtained it was unlikely that the oil shale combustion plant in Estonia is a relevant emission source for dioxins and furans or PCBs. Even though this assumption can only be confirmed with definitive certainty by stack emission measurements it was decided that the effort of a measurement campaign carried out by the measurement team of LUA would be disproportionate compared to the expectable results.

5.1.2.3. Inventory of possible dioxin emission sources in Latvia

The preliminary information of the Latvian informant provided LUA with a list of potential dioxin sources from the “Latvian Inventory on Potential Dioxin Sources”. The following table 5 gives an overview on these data:

Air Emission Source	**Available Information**	**Comments**
domestic wood combustion	> 1.500.000 m³/year	domestic combustion of preserved wood very frequent
district heating by small power plants (coal fired)	3 plants	
charcoal production	35 plants (> 20.000 t/year)	
industrial wood combustion	3 plants	furniture wood
lead production (illegal)		produced from scrap by many small companies
cement production	2 plants (1 operated at the moment)	co-combustion of different waste materials
lime production	1 plant	very small
brick and keramsite production	2 or 3 plants	
paper and cellulose production	1 plant (Ligatne)	chlorine bleaching
road transport		
municipal and hospital waste incineration	2 plants (1 plant for hospital waste only)	Riga and Jelgava region (Cena)
industrial waste incineration	1 plant	Jelgava region (Cena)
landfills	300 sites (2.500.000 m³/year)	illegal combustion of different waste materials
fires		

table 5 List of potential dioxin sources in Latvia

Considering dioxin emissions in Latvia hazardous waste incineration, clinical and municipal waste incineration, paper, illegal lead, charcoal, and cement production may be of interest.

In Latvia a 2 chamber rotary kiln is operated for hazardous waste incineration. It is running now about six years. As incinerators for hazardous, industrial waste generally must be considered as dioxin sources it did not appear necessary to analyse filter dust samples from this facility in order to assess whether there is a dioxin formation potential. The level of dioxin emissions depends on the kind of input materials (waste), the technology used, the temperatures and residence times applied and the abatement systems. From a large number of measurements carried out at rotary kilns dioxin emissions may be estimated to be in a range between 10 and 100 ng I-TEQ/m³ if usual industrial waste (e.g. solvents) is burnt. Therefore it was quite probable that the emissions from the Latvian facility would be within this range, too. Stack emission measurements would surely be required to assess the emissions with higher precision.

Yet, the EC Directive 94/67/EG [3] sets already a limit value of 0.1 ng I-TEQ/m³ for these installations. For that reason there was no urgent need for new data from this type of plant particularly because no new knowledge could be expected. The pragmatic conclusion in this case is: If Latvia joins the EC then this plant must comply with the Directive 94/67/EG [3] anyway.

However, with respect to the possible health impacts on people living in the vicinity of the incinerators it would be desirable to determine the actual emissions of dioxins and furans. The same applies to the quite unknown possible emissions from illegal lead smelters, from charcoal production and from cement plants applying the wet cement production technology using car tyres as additional fuel. For all of these facilities it would make sense to analyse filter dust samples (if there are filters at all!), chimney scrapings or slag samples. It seemed that it might have been possible to get such samples from charcoal production whereas it probably would be quite difficult or even impossible to get such samples from illegal lead smelters to say nothing of emission measurements. Nevertheless the Latvian partner institution (National Institute for Health and Environment) was asked to collect about 1 kg of filter dusts or slag materials from these types of plants for dioxin analysis. For unknown reasons this has not been done.

5.1.2.4. Survey on dioxin emissions in the Czech Republic

5.1.2.4.1. Inventory data:

The Czech Republic has set up a preliminary overall emission inventory of PCDD/F for the period of 1990 - 1998. The emission balances were processed from the available information on directly measured emission factors of Czech emission sources and capacity data (consumption of fuel, heat supplied in fuel, production of selected technologies). Other information was gained from literature sources (research reports from the 1993 - 1999 period) and from the 1st and 2nd editions of the Atmospheric Emission Inventory Guidebook. The range of emission factors was established from these data sources for individual categories of plants (sources for electricity and heat production, technological sources, waste incinerators, mobile sources). The inventory was worked out especially for categories involved in Annexes of HM and POPs protocols (see table 6).

year	1990	1991	1992	1993	1994	1995	1996	1997	1998
PCDD/F emission	2,20	2,12	2,09	1,96	1,92	1,86	1,63	1,50	1,38

table 6 Overall PCDD/F emissions in the Czech Republic — units: kg per year

5.1.2.4.2. Measurement results

The HM and POPs emission measurements were performed pursuant to Degree No. 117/1997 of the Ministry of the Environment and according to projects of the Ministry of the Environment (especially the Project VaV/520/1/97). The measurements were made at 46 sources using combustion of solid and liquid fuels for heat and electricity production, at 36 technological sources (sinter plants, grey iron foundries, steel production plants, etc.) and at 29 waste incinerators (see table 7).

Source	EF (PCDD/F)	measurement year
Sinter plants	5,76	1990(simulation)
	0,05	1997
	20,00	1998
	5,00	1998
	3,84	1999
Steel plants	4,51	1993
	40,00	1998
	35,00	1999
Grey iron foundries	0,48	1990(simulation)
	2,00	1993
	0,20	1995
	0,79	1996
	2,85	1996
	0,57	1999

domestic burning (brown coal)	205,68	1994
	251,20	1994
	188,40	1994
	188,40	1994
	123,90	1995
	6,39	1996
	8,28	1996
	3,44	1996
domestic burning (briquettes)	10,00	1995
domestic burning (coke)	3,73	1994
	5,60	1994
	4,20	1994
	13,70	1995
domestic burning (hard coal)	75,28	1994
	65,28	1994
	81,60	1994
	81,60	1994
	75,30	1995
	1,58	1996
	2,43	1996
domestic burning (wood)	0,01	1994
	0,01	1994
	8,50	1995
	0,63	1996
municipal waste incinerators	0,49	1999
industrial waste incinerators	135,00	1993
	94,78	1994
	425,71	1994
	41,51	1994
	0,01	1994
	0,56	1999
	1,10	1999
	0,19	1999
hospital waste incinerators	160,00	1993
	29,23	1994
	4,00	1998
	0,48	1999
	18,00	1999
	25,00	1999

table 7 Selected data on PCDD/F emission factors measured at relevant sources in the Czech Republic — units: µg/ton (I-TEQ)

5.1.2.4.3. Measurement programs

There does not exist a concrete measurement program in the Czech Republic. Measurements take place pursuant to Degree No. 117/1997 of the Ministry of the Environment[1] and according to projects of the Ministry of the Environment (especially the Project VaV/520/1/97).

The Czech Republic’s fundamental legislative and regulatory framework related to air pollution abatement is composed of:

Act No. 309/1991 (Clean Air Act) as later amended in Act No. 211/1994 on Air Quality Protection from Pollutants

Act No. 389/1991 as later amended in Act No. 212/1994 of the Czech National Council on State Administration in Air Quality Control and Charges for Air Pollution

Degree No. 117/1997 of the Ministry of the Environment which lays down emission limit values (emission limit values for PCDD/F still do not exist), permissible smoke darkness, a list of air pollutants, categorisation of sources, determination of emission levels and the technical means for their measurement, requirements for keeping operating records for large and medium-sized sources, and requirements for fuel quality.

---

[1] § 13 — Power Plants, Major Heating Plants and Local Heating Plants

(4) For power plants, major heating plants and local heating plants with furnaces with nominal thermal outputs of 50 MW or greater burning solid or liquid fuel, single measurements shall be carried out to determine the content in the combustion products of emissions of the heavy metals set forth in Annex No. 1 and of persistent organic substances (polychlorinated biphenyls, polychlorinated dibenzodioxins, polychlorinated dibenzofurans, polycyclic aromatic hydrocarbons) after the first bringing of the source into operation and also following each change in fuel or following each significant and permanent change in the design or equipment of the source, and such measurement shall be carried out within six months of the occurrence of one of these incidents. Measurements pursuant to this paragraph must be carried out for sources that are already in operation by June 30, 1998.

Full legislative assurance will be achieved with ratification of a new prepared Act on Air Quality Protection and Ozone Layer Protection (supposed 1.11. 2001) and with ratification of a new Act on IPPC (supposed 1.1. 2003). The Czech Republic is preparing for requirements of HM and POPs Protocols (CLRTAP).

5.1.3. Conclusion

Of the four Central European Countries which have been included into the Stage II project Poland and the Czech Republic are members of the first-step accession countries. Regarding the amount and extent of information available on PCDD/F emissions the Czech Republic appears to have the most advanced state. Measurements have been made at most relevant emission sources and abatement measures apparently have been introduced reducing the overall emissions to air by ca. 50% within the last decade.

In Poland activities regarding dioxin and furans have emerged in the recent years too. However, information could be obtained only on the sector of hospital waste incineration. Further measurements at other industrial sectors, e.g. the metallurgical industries, are likely to exist but were not submitted and could not be included in this report.

The co-operation with the two Baltic countries Estonia and Latvia was mainly restricted to some exchange of information. In case of Estonia a laboratory test could be made regarding possible dioxin emissions from the large oil-shale power plant operated there. This test revealed a very low likelihood of emissions to air or other media from this plant; according to the information obtained no other industrial sectors are considered to be relevant.

Contrarily, installations which are likely to emit dioxins and furans appear to exist in Latvia. Hence deeper insight into these sectors would be appreciable as for some unknown reason no material for laboratory tests cold be provided by the Latvian co-operating institute.

References

1. I. Holoubek, J. Kohoutek, P. Machalek, I. Dvorakova, B. Bretschneider, J. Mitera, V. Bures and M. Fara, The Emission Inventory of POPs (PAHs, PCBs, PCDD/Fs,HC) in the Czech Republic, *Dioxin 2000*, Monterey, CA, 13.-17.08.2000. *Organohalogen Compounds* **46**, pp. 51-54 (2000).
2. A. Grochowalski, PCDDs and PCDFs Concentration in Combustion Gases and Bottom Ash From Incineration of Hospital Wastes in Poland, *Chemosphere* **37**, 2279-2291 (1998).
3. Richtlinie 94/67/EG des Rates vom 16. Dezember 1994 über die Verbrennung gefährlicher Abfälle. In *Amtsblatt der Europäischen Gemeinschaften*, 1994, pp 34-45.

6. Denmark

6.1. Co-incineration of Hospital Waste with Municipal Solid Waste

6.1.1. Summary

In some EU countries e.g. Denmark hospital waste is co-incinerated with municipal solid waste; therefore a comparative emission measurement was carried out by the Danish National Environmental Research Institute NERI in order to see if the co-combustion of hospital wastes leads to an increase of PCDD/F emissions.

Under normal operation, about 15% of hospital wastes are mixed up with industrial and municipal waste. The results of the 6 measurements for dioxins and furans showed emission concentrations slightly exceeding the 0,1 ng I-TEQ/m³ value. The average PCDD/F concentration for co-incineration was 0,29 ng/m^3 with a standard deviation of 0,12 ng/m^3. The average concentration without co-incineration was 0,36 ng/m^3, with a standard deviation of 0,05 ng/m^3. Based on the above figures, no significant difference was detected between co-incineration (i.e. with hospital waste) and no co-incineration.

6.1.2. Background

As outlined in the Stage I report [1] , the incineration of hospital wastes is one of the emission source types which had been identified in Stage I as being potentially relevant for the dioxin emissions in Europe. Therefore it was intended in Stage II of the project to get some additional information about the situation in the countries considered in Stage I by carrying out emission measurements at typical plants.

While in some countries e.g. Germany and the Netherlands hospital wastes are treated in special incinerators designed for hazardous wastes, in other countries small on-site furnaces are still operated or the waste is added to conventional municipal waste incinerators. In Denmark, like mostly done in Germany, some hospital waste is also proceeded to special incinerators. A large part though (about 50 - 60 % of a total amount of 6.000 - 7.000 tons per year of hospital waste in Denmark) is co-incinerated together with MSW. These incinerators have special safe-guards to prevent the discharge of infectious material.

6.1.3. Results and discussion

The incinerator selected for the measurements is a conventional grate furnace operated without any dioxin specific flue gas cleaning systems (see figure 1). The abatement facility just consists of a conditioning with water and a fabric filter for trapping of particulate matter. Therefore it was expected, that the average dioxin emission would exceed the 0,1 ng I-TEQ/m³ value set for hazardous waste incinerators.

Under normal operation, about 15% of hospital wastes are mixed up with industrial and municipal waste (about 40% each). According to a definition of the Danish EPA hospital waste comprises of:

- healthcare risk waste, which includes waste from hospitals, maternity homes, treatment centres, home care schemes, medical practices, dental clinics, midwifery etc., which in the event of immediate contact may involve a certain risk during handling,
- cutting and prickling objects used in the care or treatment of patients,
- other infectious waste possibly containing micro-organisms from diagnostics and treatment of patients and from animals used for experiments.

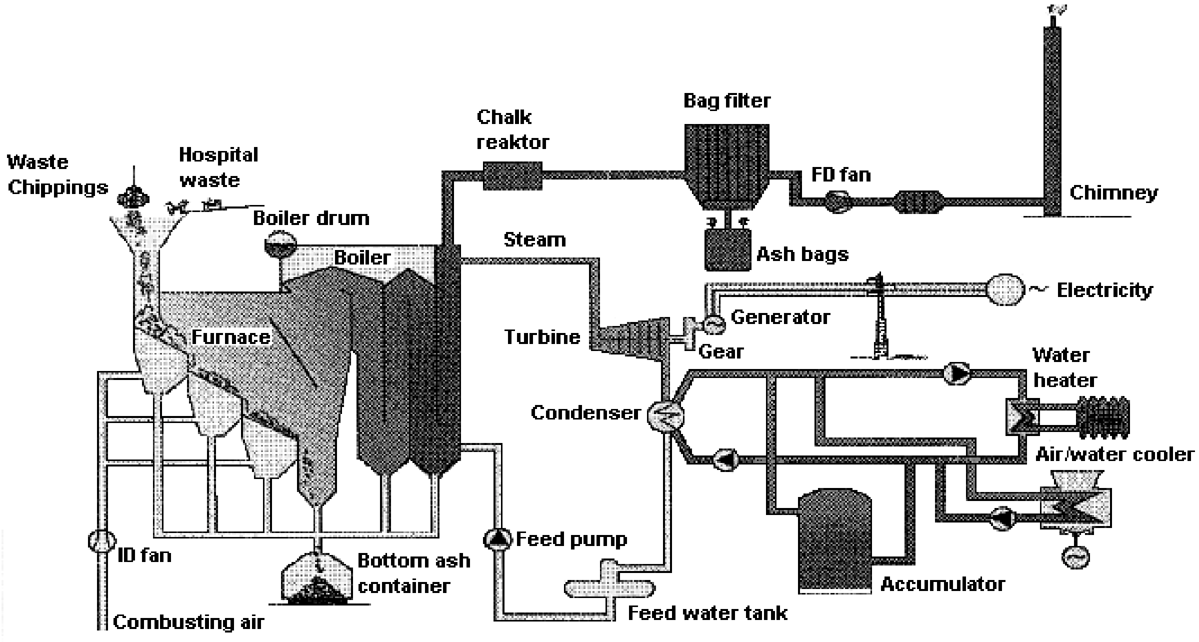

figure 1 Schematic draw of the investigated msw incineration plant (taken from [2])

For some types of healthcare risk waste such as tissue and body parts recognition of the waste after treatment is undesirable. Consequently, along with treatment by incineration large coherent tissue and body parts shall be treated separately to ensure complete burnout. Such waste is called tissue waste in this guideline. Tissue waste can be defined as all recognisable tissue and body parts as well as other waste to be treated beyond recognition for aesthetic reasons.

For safety reasons it was not possible to assess the particular composition of the hospital waste fraction burned during the emission measurements, but it is reasonable to assume, that the definition given before was applied. To assess the influence of co-combustion on the emissions of dioxins and furans, three samples were taken during normal operation (with hospital waste) and three samples during operation without hospital waste. Before the latter sampling campaign, the incinerator was operated in the same mode for two days (a longer period which would have been desirable to establish new steady state operation conditions could not be realised due to operator's demands). Details about the measurements were presented using the default report forms. It should be noted, that sampling and analyses were done as far as possible in accordance with EN 1948 standard. Good agreement between the analytical results obtained from NERI and the cross-check analysis carried out by the LUA laboratory was observed.

As expected the results of the 6 measurements for dioxins and furans (see table 1) show emission concentrations slightly exceeding the 0,1 ng I-TEQ/m^3 value. The average PCDD/F concentration for co-incineration (samples no. 1-3026 to 3-3028) is 0,29 ng/m^3 (s. d. 11% O_2) with a standard deviation of 0,12 ng/m^3. The average concentration without co-incineration (samples no. 4-3029 to 6-3031) is 0,36 ng/m^3 (s. d. 11% O_2), with a standard deviation of 0,05 ng/m^3. Based on the above figures, no significant difference between co-incineration (i.e. with hospital waste) and no co-incineration was detected (two-tailed t-test, equal variance, 90 % level of significance).

sampling no.	Actual O_2 conc. [vol %]	PCDD/F [ng I-TEQ/m³]	reference O_2 conc. [vol %]	PCDD/F at ref. O_2 [ng I-TEQ/m³]
1-3026 with hw	11,9	0,17	11	0,18
2-3027 with hw	12,2	0,24	11	0,27
3-3028 with hw	12,2	0,37	11	0,42
4-3029 without hw	11,9	0,29	11	0,32
5-3030 without hw	12,2	0,37	11	0,42
6-3031 without hw	12,4	0,30	11	0,35

table 1: results of comparative PCDD/F emission measurements at a plant for co-combustion of municipal and hospital wastes in Denmark; hw: hospital waste

Looking at operating parameters registered during the sampling no differences in the operating conditions were detected (two-tailed t-tests, equal variances, 90 % level of significance, see table 2). Except for CO the values which are based on 1 hour averages were measured with the plant instrumentation.

Parameter	Co-incineration	No co-incineration
CO (mg/m^3, 11%O_2)	11	12
Combustion temperature I (°C) Standard deviation	1040 7	1040 6
Combustion temperature II (°C) Standard deviation	1172 17	1170 8
Steam production (t/h) Standard deviation	14,2 0,4	14,0 0,2

table 2: comparison of some parameters characterising plant operation conditions during the measurement campaigns

6.1.4. Conclusions

In spite of the frequently reported findings that incineration of pure hospital wastes can lead to elevated levels of dioxins and furans co-combustion of hospital waste in a municipal waste incinerator in Denmark did not influence the emissions of that plant significantly. On one hand, this may be due to the good burn-out conditions which can be achieved better in larger incinerators than in small facilities mostly used for combustion of hospital wastes. On the other hand, a dilution effect must be taken into account as only about 10 % of the flue gas resulted from the hospital waste fed into the incinerator. The absolute emission level was found to be in the range of 0.3 ng I-TEQ/m³ and appears to be low in view of the simple flue gas cleaning system of the investigated plant.

References

1. U. Quaß, M. Fermann and G. Bröker, Identification of Relevant Industrial Sources of Dioxins and Furans in Europe, LUA Materialien Nr. 43, 936 pp., Landesumweltamt NRW (1997).
2. J. Vikelsøe, P. Blinksbjerg and A. A. Jensen, THE DG ENV EUROPEAN DIOXIN EMISSION INVENTORY- STAGE II: EMISSIONS OF DIOXINS FROM CO-INCINERATION OF HEALTH-CARE RISK WASTE AND MUNICIPAL SOLID WASTE, *Dioxin 2000*, Monterey, California, 13.-17.08.2000. *Organohalogen Compounds* **46**, pp. 232-235 (2000).

7. Belgium:

7.1. Emissions from Iron Ore Sintering Plants

7.1.1. Summary

Emissions of dioxins and furans from two iron ore sintering plants located in the Walloon part of Belgium were measured by a Belgian institute. One plant recently was reconstructed introducing a separate cooler and thus increasing its production capacity. The other plant, approx. half the size of the first, was measured under conditions which may be considered representative for the recent year's operation. Average flue gas concentrations of 0,7 ng I-TEQ/m³ and 6,8 ng I-TEQ/m³, respectively, were found. Overall annual releases from both plants ares calculated to be 28 g I-TEQ/year. Thus, together with the emissions from the two sinter plants in the Flemish part of Belgium, a release of more than 100 g I-TEQ can be estimated for the year 1995. Meanwhile this emission has declined by approx. two thirds due to primary abatement measures at the most important Walloon facility.

7.1.2. Background

One of the major new insights gained from the emission measurement programs which were carried out in several countries at the early 90s was the finding that iron ore sintering plants can be considered as the most important industrial source besides waste incineration. While for the majority of the investigated plants in Germany, the Netherlands and the United Kingdom flue gas concentrations between ca. 1 and 5 ng I-TEQ/m³ were found, some facilities were shown to have considerably higher emissions (c. f. Stage I report). The worst case known was a plant with more than 40 ng I-TEQ/m³ located in Germany.

Because the actual emission situation of a sinter plant appears to be unpredictable from considerations of operation conditions and processed materials one of the main recommendations at the end of Stage I was to initiate emission measurements at all sinter plants not yet investigated. These included the plants in Belgium, France, Italy, Portugal and Spain.

In case of the Belgian plants an agreement on emission measurements could only be achieved concerning those facilities located in the Walloon region. For Flanders the regional environmental authorities decided to carry out their own program independently of the Stage

II project. Results of these investigations have been published recently in terms of annual emission for the years 1998 to 2000 (see below).

7.1.3. Results and discussion

Within Stage II emission measurements were carried out at the sinter plants located at Liége and at Charleroi. Both belong to the steel company Cockerill-Sambre.

The Liége plant was upgraded by installation of a separate cooler in autumn 1999. Before, cooling of the sinter took place on the sinter strand thus limiting the plant’s capacity. After upgrade, the capacity increased from 12.000 to 15.000 tons sinter/day; it is intended to finally produce 17.500 tonnes per day. The upgrade also effected a change of flue gas collection and emission. In the former configuration there was one stack emitting the flue gas collected from the sintering process, from the cooling area and from the ambient air within the sinter plant. To date, flue gases of the new separate cooler are emitted through a separate stack which was not used previously. Thus, the stack where the samples were taken from comprises the flue gases from sintering (~ 1.750.000 m^3) and from ambient air (~ 500.000 m^3).

At the second plant located at Charleroi no change of operation conditions occurred during the recent years; hence, the results obtained may be considered as typical for the emissions since start-up of the plant by December 1994.

At both plants samples were taken through access ports located at the stack. These ports were accessible via platforms installed at mean-height approximately. Due to the large stack diameters and the limited length of the probes it was impossible to carry out a complete net measurement covering the entire cross section. However, as the flue gas velocity measurements indicated a reasonable profile this was not considered to challenge the results obtained.

In table 1 the PCDD/F measurement results and some operation parameters are shown. For each plant one cross-check sample was analysed at the LUA dioxin laboratory. Flue gas concentrations of 1,4 and 6,9 ng I-TEQ/m^3 were obtained for the extracted aliquots of samples 1 and 5, respectively. Both control results showed elevated values. The deviation in case of sample 1 appears quite high; this might be due to different treatment of the samples: contrary to the scheduled procedure this sample occasionally had been subjected to ISSeP's clean-up before it was sent to LUA. Hence it was analysed using the extraction standard of the Belgian lab while LUA’s extraction standard was added to the other sample.

Nevertheless the deviations appeared acceptable and no further investigations were made.

		PCDD/F ng I-TEQ/m^3	Flow rate Stdm^3/h	mass flow mg I-TEQ/h	Annual emission*) g I-TEQ/a	Production rate tonnes/h	Emission factor µg I-TEQ/t
Liége	sample 1	0,80	1.504.934	1,2	10,5		
	sample 2	0,59	1.369.811	0,8	7,1		
	sample 3	0,74	1.470.864	1,1	9,6		
	mean	**0,71**	**1.448.536**	**1,0**	**9,1**	**581,0**	**1,8**
Charleroi	sample 4	9,50	366.608	3,5	30,5		
	sample 5	5,83	383.271	2,2	19,6		
	sample 6	5,15	389.948	2,0	17,6		
	mean	**6,82**	**379.942**	**2,6**	**22,5**	**289,0**	**8,9**

table 1 PCDD/F emission from the two Belgian sinter plants measured within the Stage II project
***) for 8000 hours per year**

There is nearly a factor of 10 between the flue gas concentrations of the two plants which correspond to emission factors differing by a factor of 5. Another parameter correlating with this difference in PCDD/F emissions is the dust concentration which ranged from 29 to 61 mg/m^3 at the Liége plant and from 61-167 mg/m^3 at the Charleroi installation. Whether further operation parameters may have caused the observed differences is currently subject of internal discussions between the plant operator and ISSeP.

As mentioned above no co-operation on measurements to be carried out within the EU project was achieved with the Flemish steel industry or public environmental institutes, respectively. However, emission estimates submitted for the years 1998 and 1999 indicate that the emissions from sinter plants in Belgium had been underestimated considerably. The two sinter plants in Flanders were shown to have following emissions:

- 1998: 80,7 g I-TEQ/a
- 1999: 20,3 g I-TEQ/a
- 2000: 7 g I-TEQ/a foreseen on the basis of actual measurements,

- 2001: 5 g I-TEQ/a estimated by the plant operator (Sidmar). The plant operator claims to be able to obtain the emission guide value concentration of 0,4 ng I-TEQ/m³. This would result in an annual emissions of 3,8 g I-TEQ/a.

Together the four Belgian plants are likely to have caused emissions of more than 100 g I-TEQ/year in the recent years. This supports the view that for the year 1995 the default overall emission factor of 10 µg TE/ton sinter (yielding 98 g I-TEQ/year annual emission for Belgium) chosen in the Stage I report appears to be a quite good estimate. As one of the Flemish plants was identified to be the major emitter (up to 20 ng I-TEQ/m³ were reported [1]) immediate action was undertaken to reduce the emissions from this installation. Accordingly, the emissions from the Flemish installations have decreased by more than 90% until now. Moreover, the operator of the Flemish sintering plants has joined the international consortium which has build a pilot sintering facility with state-of -the-art abatement installations (active carbon injection/catalyst).

7.1.4. Conclusion

The results obtained form the measurements carried out within the Stage II project as well those reported from the Flemish emission testing program clearly support the relevance of iron ore sintering for the European dioxin emissions to ambient air. The improvement achieved within short time after measurements had shown the high emissions at the most important of the four plants also indicates that measurements are necessary to convince plant operators that they have to consider further actions.

References

1. F. Francois, P. Bernaert and R. Baert, Reduction of the PCDD/PCDF Emissions in the Flemish Region (Belgium), *Dioxin 2000*, Monterey, California, 13.17.08.2000. *Organohalogen Compounds* **45**, pp. 352-355 (2000).

8. Germany:

8.1. Dioxin Emissions from Cold wind Cupola Furnaces in Iron Foundries

8.1.1. Background

In the Stage I report "Identification of Relevant Industrial Sources of Dioxins and Furans in Europe" [1] several emission sources were identified — belonging to the basic metal industry — which contribute relevant amounts of PCDD and PCDF to the total emission of dioxins and furans in Europe. According to available data and aside from the very important iron ore sintering plants, the less important electric furnaces used in steel production and a number of various processes in the non-ferrous metal industries play a remarkable role. All metallurgical processes emitting polychlorinated dibenzodioxins and dibenzofurans (PCDD and PCDF) in non-negligible amounts appear to use not only input materials composed of ores and additives from natural resources but also of secondary, differently contaminated scrap materials, residual matters from preceding process steps and production residues.

Another process in the iron and steel industry which fits into this criterion is the smelting process in cupola furnaces for the production of cast iron and cast steel. To this process various amounts of scrap are added depending on the desired product and quality; this practice of which purpose it is to save raw materials by re-circulating waste materials has certainly beneficial effects on the environment. When phase II of the EU dioxin project was started very little was known about the dioxin emissions from cupola furnaces operated in iron and steel foundries. The report "Establishing the Requirements for Limiting the Emissions of Dioxins and Furans" published by the LAI in 1995 [2] contained the results of measurements taken at only 3 hot-blast and 2 cold-blast cupola furnaces. While the concentrations in the waste gas of the hot-blast cupola furnaces were below 0,1 ng I-TEQ/m^3 in all measurements, they amounted to a range of barely below 0,1 to about 0,5 ng I-TEQ/m^3 in the waste gases of the two cold-blast cupola furnaces. In one cold-blast cupola furnace operated in the German state of Saxony-Anhalt concentrations of up to 1 ng I-TEQ/m^3 were measured in the waste gas flow between two scrubbers [3].

Only a few reliable measurement results of cupola furnaces were found form other countries as well. The “Swiss Manual on Emission Factors” [4] provides a value of 3,5 µg I-TEQ/ton of iron smelted in cold-blast cupola furnaces; this emission factor is based on measurements at 2 plants. In Sweden one cupola furnace was studied during a dioxin survey [5]. This furnace, equipped with a high-pressure scrubber and a recuperator for waste-gas afterburning, emitted only extremely low amounts of PCDDs and PCDFs in the waste gas. Due to the high concentrations of dioxins in the sludge of the scrubber, which were estimated to amount to 390 mg N-TEQ/a, a high emission potential was assigned to this plant.

8.1.1.1. Process Description

8.1.1.1.1. Melting of cast iron in cold-blast cupola furnaces

Primarily foundries use scrap iron and scrap steel as input material aside from pig iron and internally re-circulated material for the production of cast parts made of iron and steel. Scrap of defined quality classes is obtained from scrap dealers or to some extent also from the producers e.g. in the case of waste material from punching of metals. Because only manageable sizes of material fit into a cupola furnace, the scrap must be comminuted before it is recycled. Almost always the scrap dealers take care of the comminution. The foundry receives from them the so-called "cast scrap".

The applied pig iron is a special, high-carbon containing type of pig irons which is exclusively produced in a blast-furnace process in Germany by the company DK Recycling und Roheisen GmbH.

The internally recirculated material consists of re-useable waste material produced in the foundries themselves. This kind of waste material includes defective cast parts and, more important, spouts and feeders left over in the production process from the filling systems of moulds. This valuable material possesses the desired quality and is perfectly suitable for a renewed melting process. While cast scrap consists of different materials (with the exception of first quality scrap), which may include parts with surface finishing or contaminants, internally recirculated material is approximately as pure as the produced cast iron (or cast steel) because it went already through the cupola process once.

Such quality is generally not available on raw material markets. Moreover, it would undermine the basic idea of the recycling law if only peak quality (cast) iron scrap was used in the recycling process.

Germany:Dioxin Emissions from Cold wind Cupola Furnaces in Iron Foundries

Cupola furnaces are primarily used for smelting of the input material and producing cast iron. These coke-heated vertical furnaces are charged batch-wise with raw materials, or sometimes continuously via vibrating chutes. The necessary heat for smelting of the charged materials is produced by means of coke combustion and air blown in through tuyeres at the sides of the furnace. The actual smelting zone is found in the lower third of the vertical furnace. The furnace is not extinguished after every new charge of raw material; it is re-charged in batches of raw material instead, with a speed depending on the decrease of liquid iron and the temperature conduction in the furnace. With regard to heat utilisation the operation is not different from familiar coal-fired stoves at home.

While liquid iron leaves the smelting zone and flows towards the bottom of the cupola furnace, new raw material moves down from the top. The smelt is separated in a siphon or in a cupola well from the lighter liquid slag and flows to a receiver or is tapped off from time to time. It then proceeds to casting equipments or pouring ladles. The smelting capacity (t/h) depends mainly on the air volume blown in for combustion, the amount of fuel and the diameter of the furnace.

As mentioned before, the air for combustion is blown in through tuyeres. Cold-blast cupola furnaces may be equipped with one or two rows of tuyeres. In cupola furnaces with secondary air injection, carbon monoxide — which develops in every cupola furnace — is partly burned by the injected additional amount of air using the available combustion heat:

$$CO + O_2 \rightarrow 2CO_2 + heat$$

Most of today’s cold-blast cupola furnaces have the possibility of blowing in oxygen. After a shut-down such furnaces are capable of reaching the required tapping temperature faster and the smelting capacity of such furnaces is higher.

8.1.1.2. Combustion process and formation of waste gas

In the smelting zone above the tuyeres level coke is burned by the air blown in thus providing the energy for the smelting process. The smelted iron and the forming slag — which mostly consists of silicates — flow finely distributed over the glowing coke into the cupola well. The temperature in the cupola well is about 1500 °C, in the gas residing in the smelting zone a considerably higher temperature prevails (see air/waste air temperature profile of a cold-blast cupola furnace).

Germany:Dioxin Emissions from Cold wind Cupola Furnaces in Iron Foundries

The combustion gases streaming upwards through the furnace heat the downward moving charge of iron, coke and limestone. Directly above the smelting zone at temperatures of > 800 °C carbon dioxide is reduced by coke. This reaction consumes energy which cools the gas. The remaining heat preheats the charged material in an oxygen-free reducing atmosphere. The so-called top gases or waste gases are drawn off in cold-blast cupola furnaces above the charge in the upper part of the furnace and are passed to a dust collection system which consists in the studied furnaces generally of a cyclone, a cooler and a cloth filter.

The input material as well as coke and limestone are charged through an opening in the top. In order to avoid any escape of waste gases through this opening a powerful ventilator is running generating a slight under-pressure in the opening which prevails during all operating conditions. Through the entrained air, oxygen concentrations of 15 to 18 % are usually measured in the waste gas stack. Because undiluted waste gas usually contains no oxygen a dilution of 1 to 3,5 till 7 is obtained from these percentages.

Due to the CO content, the waste gases may be ignited by the entry of air (top fire). Top fire also occurs during blow down and in furnaces with a relatively low height of the charged material column.

The smelted iron takes up carbon and sulphur from the coke and gives up undesirable contamination such as oxides, silicates and other salts to the slag. Primarily, accompanying substances with high oxygen affinity are taken up by the slag. Particles adhering to the scrap and fines from coke and limestone are carried off with the dust in the waste gas and are collected in the cyclone, cooler and filter. Because of their relatively high volatility, chlorides are mainly found in the dust.

The emitted amounts of dust are usually low. A filter cake is formed on the cloth filter by the dust in the waste gas, which must be removed from time to time to limit the differential pressure of the filter. However, filter cake removal is never complete during the entire operation of the ventilator so that dust leaves the filter with the waste gas. As the felts used in cloth filters usually can only bear temperatures of 130 to 160 °C at the most, the waste gas temperature usually needs to be limited to even below 100°C. This is achieved by indirect cooling with air, heat exchangers, water injection or addition of fresh air.

8.1.1.3. Foundries in Europe

According to "Panorama of the EU Industry" [6] approximately 8 million tons of cast products were produced in the EU in the year 1993. The amounts smelted in cupola furnaces to produce these cast products are unknown. Because cupola furnaces generate the lowest energy costs the amounts smelted in cupola furnaces are probably considerable. However, the increasing emphasis on quality, the declining amount of produced grey cast iron and as a consequence of that the increase in spheroidal graphite cast iron have caused many foundries to change over to electric furnaces. Of the entire output of this branch 93% is produced in a total of about 1500 foundries in only 5 EU countries, in Germany (40%), France (17%), the United Kingdom (15%), in Italy (14%) and Spain (7%). The exact number of cupola furnaces in the foundries of these countries is unknown but it is estimated that there are several hundreds throughout Europe.

In view of the very scarce data and the relatively high number of plants in the state of North Rhine-Westphalia (North Rhine-Westphalia has 32 cold-blast cupola furnaces) the state administration had commissioned an extensive, 3-stage programme in the years 1997 to 1999 in co-operation with the foundry industry. This programme involved the collection of design data of all plants, the analysis of PCDDs and PCDFs in the filter dusts of selected plants and (based on the gained information) measurements of dioxin emissions in 6 plants. The investigations aimed at determining the parameters which influence the concentrations of dioxins in filter dusts and in waste gases and as far as possible at establishing the correlation between the concentrations of the dioxins in waste gases and the collected dusts. The findings would make it feasible to estimate dioxin emissions by the less costly analyses of filters dusts.

8.1.1.4. Extent of the Investigations:

- collection of data of 25 cold-blast cupola furnaces
- analysis of PCDDs and PCDFs in one dust sample per furnace taken from the filters as well as further parameters which are of relevance for the formation of dioxins (such as the concentrations of heavy metals and chloride)
- measurements of temperatures of the coolers and in the top of the furnaces during one complete smelting procedure
- analysis of 6 further dust samples collected from the filters at the moment when top fire occurred during the blow-down phase (was subsequently included into the programme upon request by LUA)
- classification of the furnaces according to the concentrations of PCDDs and PCDFs in the filter dusts into 3 categories:

  – category I: <0.1 µg I-TEQ/kg
  – category II: 0.1-1.0 µg I-TEQ/kg
  – category III: >1.0 µg I-TEQ/kg

- repeated analysis of PCDDs and PCDFs in the filter dust collected at one furnace for each category to verify whether the assignment to one of the 3 categories is repeatable or not (subsequently included into the programme upon request by LUA)

- PCDD and PCDF emission measurements at 6 furnaces:

- planned:	2	per category
- carried out:	2	measurements in category I
	3	measurements in category II
	1	measurement in category III

at one furnace one measurement was taken by LUA in addition to samples taken by IfG. All measurements were carried out according to DIN EN 1948.

- evaluation of the obtained data with regard to operational influences on the dioxin emissions and, if needed, statement of requirements for reducing emissions and of reducing possibilities.

8.1.1.5. Summary of Results

8.1.1.5.1. Design and waste gas temperature

The cold-blast cupola furnaces studied vary widely with regard to design and operating conditions. An evaluation of the data collected from the furnace operators yields the following result:

1. The smelting capacities of cold-blast furnaces range from 2.5 to 14 t/h.
2. Smelting takes 300 to 3400 hours per year.
3. Three furnaces blow secondary air through the charge.
4. Only one furnace has an alkaline lining.
5. Thirteen furnaces can inject oxygen.
6. Three furnaces produce top fire during normal operation .
7. In all furnaces the waste gas is drawn off in the top and passed through a dry dust collector (filter).
8. No cast scrap is generally used in the charge which is smelted to produce malleable cast iron.

9. In four furnaces solely charges to produce malleable cast iron are smelted and in one further furnace such charges are occasionally smelted.
10. Three furnaces have the option of recycling the dust collected from the top gas to the smelting zone.

The temperature recordings at the top of the furnaces and ahead of the coolers revealed that smelting runs can be quite different in the various cupola furnaces. During heating the temperature rises in all furnaces. During normal operation the waste gas temperatures in the top depend on:

- whether operation includes top fires or not
- whether down-times occur
- the height of the cupola furnace
- the amount of coke applied
- the intensity of the blast
- and the size of the charge maintained in the furnace.

The waste gas temperatures were measured in all cupola furnaces on the day the dust samples were collected from the filters. Because all furnaces are equipped with dry dust collectors, the waste gas temperatures in the waste gas stack are by necessity below 160 °C, in most cases even below 100 °C.

The frequency distributions of the temperatures measured in the various furnaces differed clearly from each other reflecting the differences between the various operating conditions. Peak temperatures of up to 800 °C were measured with most of the values lying between 100 and 500 °C.

8.1.1.6. PCDDF-Concentration in the collected filter dusts

The dust samples were taken from the outlet to the collector (which in most cases was a big bag). Sampling lasted about 15 minutes in each case.

Because it was assumed that the chemical composition of the filter-collected dust depended on whether the furnace was operated with or without top fire a second dust sample was drawn in the blow-down phase in furnaces in which no or very little top fire occurred during normal operation. Such samples — taken in six furnaces — were separately analysed.

The concentrations of the dioxins and furans in the filter-collected dusts had a range of values covering more than 2 orders of magnitude, 0,03 to 12,4 µg I-TEQ/kg dry mass (see figure 2). Most of the samples (19) contained concentrations between 0,1 and 1µg I-TEQ/kg (category II); 7 samples had lower values (category I), 8 samples had higher values (category III).

An assessment of the environmental and occupational relevance of the concentrations found can be done using the limit values given in the German ordinance on prohibition of certain chemicals (Chemikalienverbotsverordnung) and the ordinance on dangerous substances (Gefahrstoffverordnung). According to the latter special actions are to be undertaken by the operator of a plant, if substances or materials handled in the process are contaminated with polyhalogenated dioxins and furans at levels above 100 µg/kg (absolute concentration, not TEQ). This condition is not fulfilled in the case of the filter dust investigated in this study.

The second ordinance mentioned does not allow to sell or trade materials which contain summed-up dioxin concentrations exceeding giving limit values (see table 1**)** An evaluation of all dust samples taken in this subproject shows, that samples which fall into category III always, and also those samples of category II having I-TEQ higher than about 0,45 µg/kg exceed the limits. Thus, 15 of the 40 collected dust samples would not be allowed to be traded.

Furthermore, comparing to the guide value of 0,1 µg/kg I-TEQ which is discussed in Germany as intervention limit for remediation of children playgrounds most of the dust samples must be considered as contaminated.

Germany:Dioxin Emissions from Cold wind Cupola Furnaces in Iron Foundries

Group to assess	Congeners	Limit values µg/kg *)		
		Sum of Group 1	Sum of group 1+2	Sum of group 1+2+3
1	2378-TetraCDD 12378-PentaCDD 2378-TetraCDF 23478-PentaCDF	1		
2	123478-HexaCDD 123678-HexaCDD 123789-HexaCDD 12378-/12348-PentaCDF 123478-/123479-HexaCDF 123678-HexaCDF 123789-HexaCDF 234678-HexaCDF		5	
3	1234678-HeptaCDD OctaCDD 1234678-HeptaCDF 1234789-HeptaCDF OctaCDF			100

table 1: PCDD/F and limit values listed in the German Ordinance on the Prohibition of Certain Chemicals
***) calculated from congener concentrations, not from TEQ values**

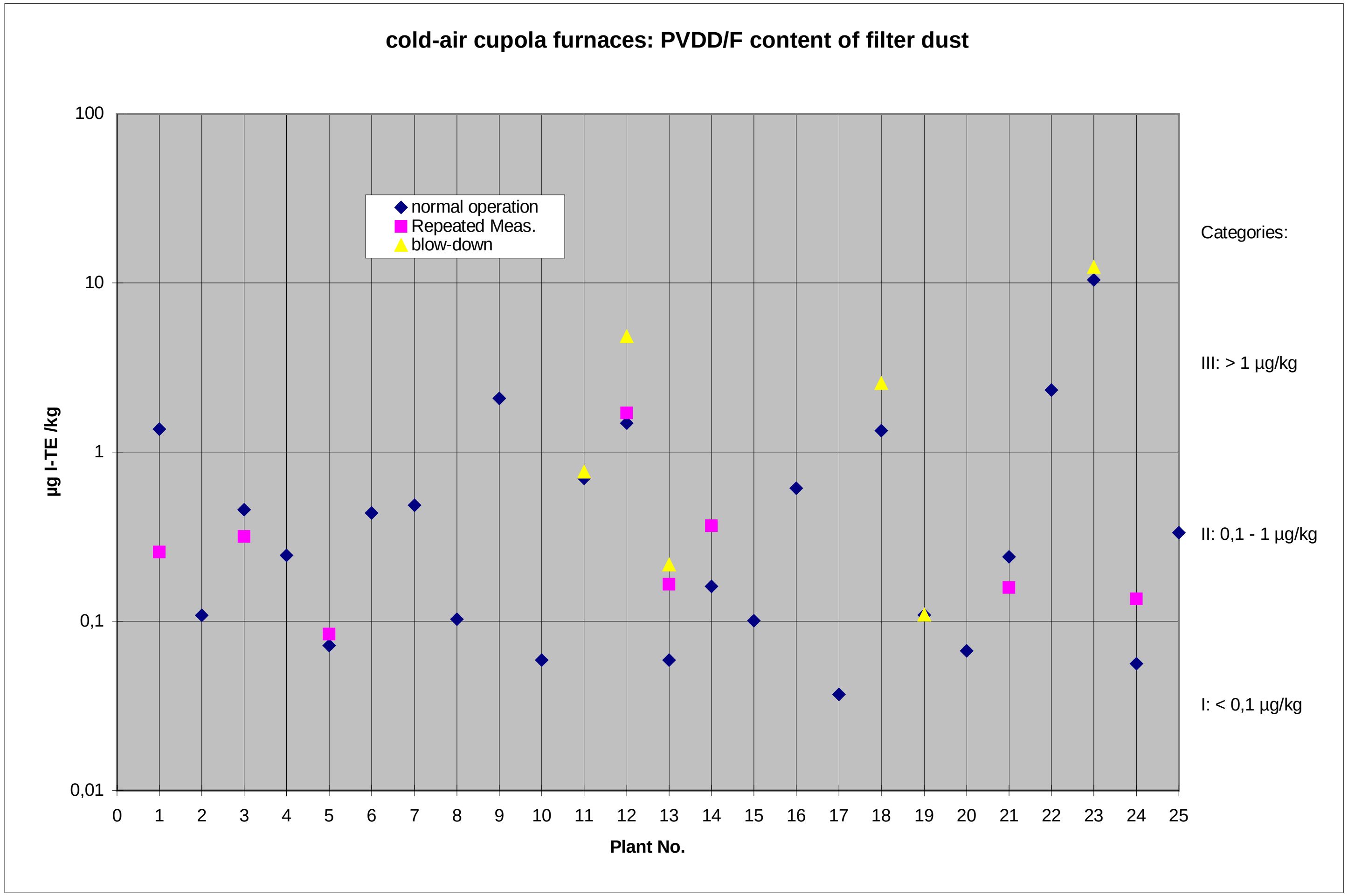

figure 2: PCDD/F concentrations in filter dust collected from 25 cold-wind cupola furnaces located in North Rhine Westphalia, Germany

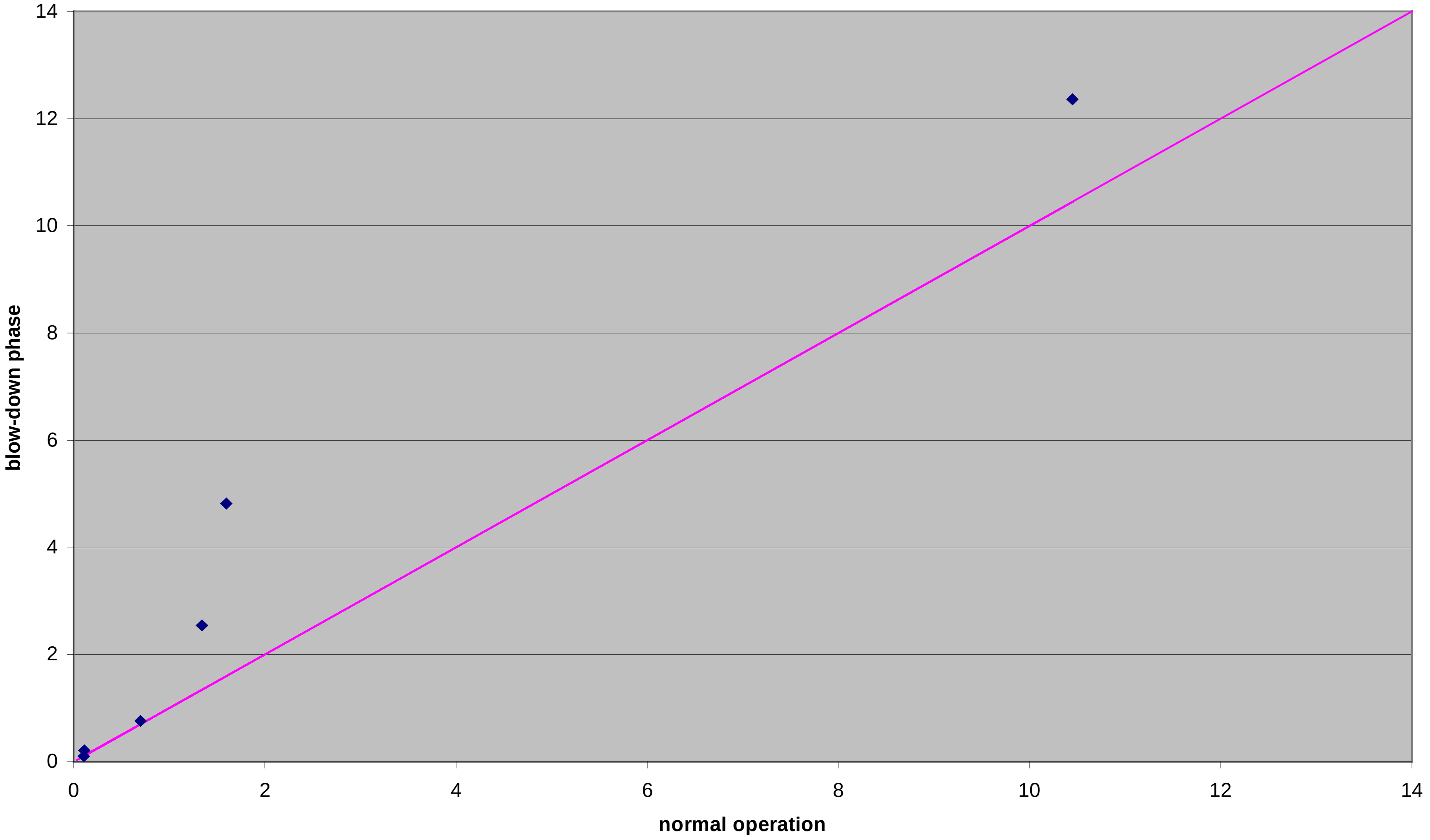

figure 3: Comparison of PCDD/F-concentration [µg I-TEQ/kg] in filter dust collected during normal plant operation and blow-down phase with top-fire

Germany:Dioxin Emissions from Cold wind Cupola Furnaces in Iron Foundries

In order to obtain information on how constant the concentrations of PCDDs and PCDFs in the filter-collected dust were in the long run, samples taken about 3 months later in 3 furnaces (one for each category) were analysed. The low and medium-high concentrations agreed well with the earlier obtained values. During the renewed measurement the furnace with a high concentration in the filter-collected dust produced a value which also belonged into category III but was lower by a factor 4 than the earlier measured value.

The comparison of dust samples — taken in 6 furnaces — during normal operation with those taken during blow-down yields no uniform results (figure 3). In three samples taken during blow-down the dioxin concentrations were clearly higher, the other three samples showed no or only a slight increase. The increase of the concentrations of dioxins during the blow-down phase coincided with an increase of the concentrations of chloride, nickel, copper and manganese in the filter-collected dust which was not observed in the cases where the concentrations of the PCDDs and PCDFs remained unchanged. This finding points at an increase of the catalyticly accelerated formation of dioxins.

No clear explanation could be found for the lower dioxin contamination in filter dusts of plants producing malleable cast. Due to the high tapping temperature required for the smelted material to produce malleable cast iron a higher coke charge is normally used than in smelting cast iron and in smelting the charge needed to produce spheroidal graphite cast iron. An evaluation of the plant data shows, that in malleable-iron foundries the coke charge amounts to 14,1% while other foundries operate with a coke charge of 11,3%.

A higher coke charge influences several parameters involved in the formation of PCDDs and PCDFs simultaneously:

- more chloride is entered into the process (on the average 25 % in the studied malleable-iron foundries)
- the furnace and waste gas temperatures are increased and
- top fire is enhanced.

A dust sample coming from a cupola furnace operated without coke (the only one in Germany and not located in North Rhine-Westphalia), which was examined for comparison, yielded with 0,068µg I-TEQ/kg dry mass a low concentration of dioxins which falls into category I (for statistical reasons it was not included in that category).

Aside from the coincidence described above only low correlation (coefficients between 0,3 and 0,4; other parameters < 0,2) between the concentrations of PCDDs and PCDFs and the concentrations of other substances (chloride, copper, nickel) in the collected filter dusts were obtained. The coke charge and the frequency of occurrence of high temperatures in the top of the furnace did not influence the concentrations of dioxins in a way which would reveal a trend.

8.1.1.7. Emission measurements

According to the category into which their concentrations (found in the filter-collected dust) of PCDDs and PCDFs fell, six furnaces were planned to be selected for dioxin emission measurements (2 furnaces in each category). Due to design (missing or inaccessible measuring points), and operation (smelting period was too short) and to a short-term shut-down of a furnace, this strategy failed. In the end only one furnace in category III was obtainable, however, 3 furnaces in category II (in settlement for the lack in category III) were available for the measurements in addition to the 2 furnaces in category I. Regrettably, the furnace with the highest concentrations in the collected dust (12 and 3µg I-TEQ/kg) could not be included. The only available furnace falling into category III had concentrations in the filter-collected dust of somewhat above 1µg I-TEQ/kg.

During the measurements the furnace was continuously monitored. In the cleaned gas random samples were taken to determine the concentrations of:

- PCDDs and PCDFs
- chloride
- dust and the dust components: Ni, Cu, Mn, V,
- organically bound carbon.

The samples were taken at the measurement port provided in the waste gas duct. Continuous measurements were carried out for:

- organic carbon using the FID,
- carbon dioxide, oxygen and carbon monoxide and the

- the waste gas temperature at the measurement port and - where possible - in the top of the furnace.

A survey on the measurement methods applied is presented below:

- PCDDs and PCDFs according to DIN EN 1948 Parts 1 to 3,
- chloride according to VDI 3480, Part 1, by photometry after sorption in bidistilled water,
- dust according to VDI 2066, Part 7, with plane filter and gravimetry,
- dust components according to VDI 2267, Part 5, treatment with HNO_3/HF and ICP spectrometry,
- organic carbon according to the sorption method in VDI 3481, Part 2, sorption on silica gel and coulometry after combustion,
- continuous gas analyses with IR-single beam photometer for CO, CO_2,
- O2 continuously with Servomex analyser using paramagnetic susceptibility,
- continuous temperature measurement with thermocouples
- organic carbon with FID, VDI 3481, Part 1, taking into consideration VDI 3481, Part 3E, 3481, Part 6 and DIN/EN 12619 E,
- data recording with data logger CSM type 12 DTL with file format Excel,
- air velocity with fan-wheel anemometer or pitot tube and micromanometer,
- static pressure with pitot tube and micromanometer,
- humidity in waste gas with wet-bulb NTC sensor and by gravimetry after adsorption on silica gel
- weather data: barometric pressure with precision aneroid barometer,
  temperature with temperature sensor Ni-CrNi,
  relative humidity with NTC sensor.

In a total of 18 individual samples concentrations between 0,003 and 0,184 ng I-TEQ/m³ were found in the waste gas; four of the furnace averages, which were obtained from three samples in each case, were below the limit value for municipal waste incinerators of 0,1 ng I-TEQ/m³.

The concentrations in emission samples taken by LUA and IfG at the same time in one plant agreed well with each other.

13 of the total 18 samples included the blow-down phase. The 5 samples which were taken during normal operation stem only from a total of 4 furnaces for which it became feasible to conduct a comparison of the results obtained with and without blow-down phase. This comparison revealed no general trend; in 2 furnaces the emission of dioxins increased when the blow-down phase was included, in the other furnaces the concentrations in the waste gas diminished. A weak correlation with the concentrations of dioxins in the waste gas was also found for all other studied parameters (temperature distribution in the top of the furnace, gas composition, dust components, amounts of coke and limestone charged). A positive correlation with the emissions was obtained solely for increased concentrations of manganese in the filter-collected dust (correlation coefficient 0,55) and an increasing amount of cast scrap. Because a reduction of the amount of cast scrap added to the charge is accompanied by a compensating increase of internally recirculated material a negative correlation is inevitably obtained between the emissions of dioxins and the amount of applied internally recirculated material.

A comparison of the concentrations in dust samples collected in the filters during the emission measurements with the found concentrations of PCDDs and PCDFs in the waste gas (both values in TEQ) provides evidence of a positive correlation (with the exception of one furnace of which set of values deviated very much from all other sets of values see figure 4). The wide range of operating conditions — to which each furnace is subjected — is reflected, for example, by the differences of the frequency distributions of temperatures and differing concentrations of PCDDs and PCDFs in the filter-collected dust obtained on the various measurement days. Due to the few emission measurements, it is not feasible to derive a relationship between the concentrations of PCDDs and PCDFs in the filter-collected dust and the concentrations of PCDDs and PCDFs in the waste gas which could be applied for a prediction of PCDD and PCDF emissions.

Germany:Dioxin Emissions from Cold wind Cupola Furnaces in Iron Foundries

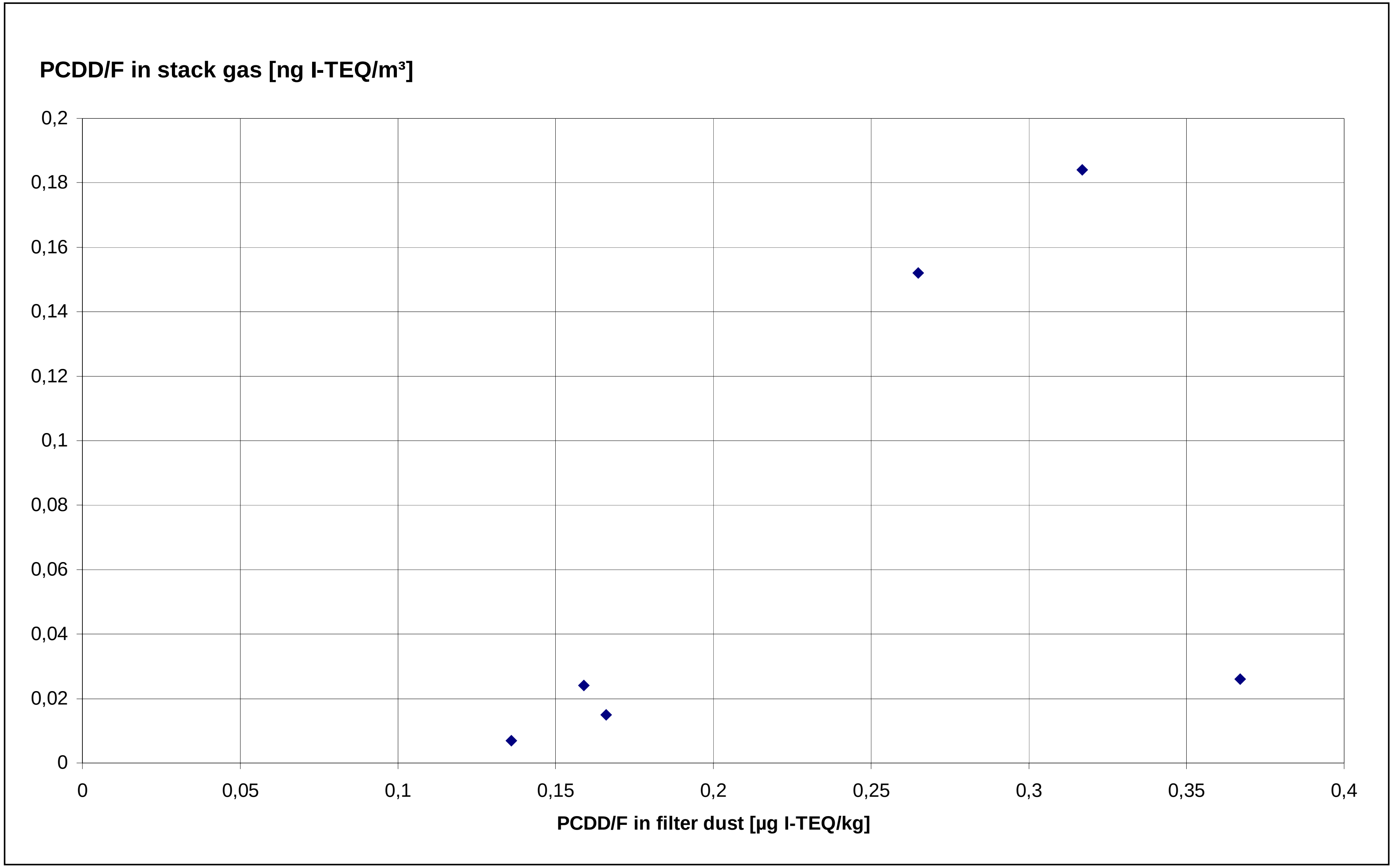

figure 4: Correlation between PCDD/F concentration in stack gas and filter dust

8.1.1.8. Estimation of the emissions from furnaces operated in North Rhine-Westphalia

The annual emissions of dioxins by cold-blast cupola furnaces operated in North Rhine-Westphalia can be determined from the concentrations measured in the waste gases and the obtained emission factors from the quantities of produced cast iron. For all furnaces studied the average emission factor was found to amount to 0,35 µg I-TEQ/t of smelted iron in the furnaces with a maximum value reaching 1,45 µg I-TEQ/t. From an annual production of 205.000 tons per year the amounts emitted per year are calculated to be 72 mg I-TEQ (average annual emission) and nearly 300 mg I-TEQ (maximum annual emission). The obtained emissions factors were markedly below the values stated in the Swiss Manual of Emission Factors.

8.1.1.9. Possibilities of reduction

Primary and secondary reduction methods will be discussed. A reduction of the amount of coke which would reduce the chlorine input (by 40 % at the most) is feasible but it is connected with high capital expenditures. Influencing the quality of the used scrap is in view of the shortage of this input material and the intentions of the recycling law not a practicable method. As secondary measures the use of activated carbon adsorption units and also of wet waste gas cleaning appears applicable; however, both methods are connected with high capital expenditures and operating costs. No findings are presently available on the suitability of a newly developed catalytic filter material which has already been tested successfully in aluminium smelting plants.

8.1.1.10. Conclusions

Looking at the concentrations found in the waste gases cold-blast cupola furnaces operated in iron and steel foundries cannot be considered as important sources of dioxins and furans due to their emitted total amounts of PCDDs and PCDFs. Thus, the results of the measurements agree with a few known data that existed before the investigations were started.

Note however, that the emissions for North Rhine-Westphalia were extrapolated from only 6 furnaces. It cannot be said with certainty that these furnaces are representative for all cold-blast cupola furnaces operated in Germany. Within this project one furnace was found having

PCDD and PCDF concentrations in the filter-collected dust of up to approximately 12 µg I-TEQ/kg. This is considerably higher than from those plants where emissions were measured (highest concentration in the filter-collected dust from these plants was 0,4 µg I-TEQ). In addition, a high temporal fluctuation of PCDD and PCDF concentrations in the filter-collected dusts became apparent. Therefore, despite of an indication of a positive correlation between the concentrations in the filter-collected dust and the concentrations in the waste gas — obtained from measurement results — it is not allowed to assume that this correlation may be extrapolated on furnaces with higher concentrations in the filter-collected dusts. For clarification, a further study programme would be necessary which, for example, would allow measurements of PCDD and PCDF concentrations in the filter-collected dust of a furnace over a longer period of time.

From the observed interdependence of PCDD and PCDF emissions and the amounts of cast scrap and recycled material applied it can be concluded that the contaminants adhering to the cast scrap (remnants of paint, oils etc.) have an influence on the emissions. In order to reduce dioxin concentrations a decrease of the amount of cast scrap would make sense, however, this would considerably reduce the cost efficiency of foundries. The question arises, whether certain contaminants on the cast scrap play a major role in the development and emission of PCDDs and PCDFs. If this is so, it would require a selective elimination from the charged input material.

Germany:Dioxin Emissions from Cold wind Cupola Furnaces in Iron Foundries

References

1. U. Quaß, M. Fermann and G. Bröker, Identification of Relevant Industrial Sources of Dioxins and Furans in Europe, LUA Materialien Nr. 43, 936 pp., Landesumweltamt NRW (1997).
2. LAI, Determination of Requirements to Limit the Emissions of Dioxins and Furans, UBA-Texte 58/95, 151 pp., (1995).
3. Dioxinbericht des Landes Sachsen-Anhalt, 115 pp., Landesamt für Umweltschutz Sachsen-Anhalt (1996).
4. Handbuch Emissionsfaktoren für stationäre Quellen -Ausgabe 1995, 341 pp., Bundesamt für Umwelt, Wald und Landschaft (BUWAL), econcept, Zürich (1995).
5. C. De Wit, K. Lexén and M. Strandell, The Swedish Dioxin Inventory: Levels, Sources and Trends of Dioxins and Dioxin-Like Substances in the Swedish Environment, Part 2 (Draft Version), Institute of Applied Environmental research, Stockholm University, Sweden (1996).
6. Eurostat, Panorama der EU-Industrie 1994.;, pp 7-15.

9. Germany

9.1. Emissions from titanium dioxide production

9.1.1. Summary

Dioxin emission measurements were carried out at the waste gas duct of a factory producing titanium dioxide. Using a modified cooled-probe method for sampling due to extraordinary high flue gas temperatures only blank values were found by the GC/MS analysis. Thus no dioxin emission to ambient air was found to occur at this plant.

9.1.2. Background

9.1.2.1. Process description

Titanium dioxide (TiO_2), a widely use pigment, may be produced by the so-called “sulphate-“ or “chloride-“ processes, respectively. In the sulphate process titanium ores are extracted by concentrated sulphuric acid; “Dünnsäure”, a final production residue of this process became of public concern some years ago with regard to the - meanwhile stopped - practice of sea-dumping. Most production sites in the world are using this technology.

In the chloride process (see figure 1) TiO_2 is produced from titanium (rutil) ore in a multi-step process by first converting the natural TiO_2 in the ore to titanium tetrachloride ($TiCl_4$) in a batch process using petrol coke, elementary chlorine and oxygen. The reaction takes place at 800-1200 °C. The off gas of this batch reaction contains gaseous $TiCl_4$, iron chloride and other metal chlorides, carbonaceous dust and a number of sulphur compounds like COS. The flue gas is cooled then by injection of raw $TiCl_4$ (taken from the condensing step) and transferred to the de-dusting facility (cyclone). The collected dust is extracted with $FeCl_2$-solution; the solid residues are mainly composed of carbon particles which are sold to the market as a fuel material with low combustion heat.

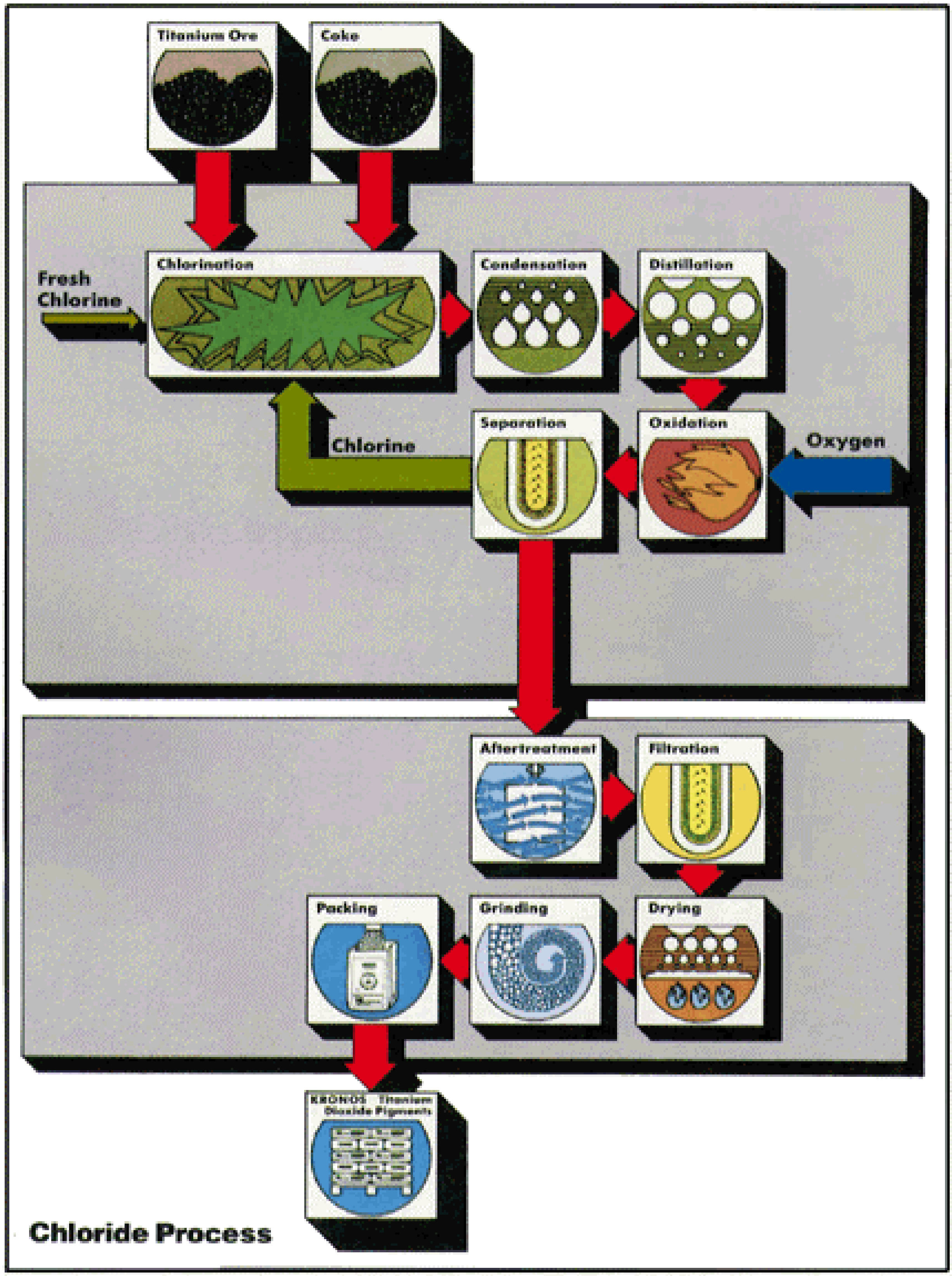

figure 1: Scheme of the chloride process for TiO_2-production (taken from www.nl-ind.com)

The flue gas leaving the cyclone is condensed to yield the raw $TiCl_4$ and then washed twice (acidic solution/$FeCl_2$-solution). Sulphur containing compounds are extracted from the off gas by catalytic reduction to elementary sulphur. Finally, the flue gas, still containing up to 50% CO, is burnt in an afterburning unit from where it proceeds to the stack.

In a separate line the raw $TiCl_4$ is cleaned and –after further pre-treatment – combusted with oxygen to the desired product, TiO_2-pigment. Chlorine is recovered from this stage and recycled to the chlorination process.

According to a 1988 compilation of TiO_2-producers [1] the chlorine process is mainly used in companies located in the United States. One factory each is listed for Canada, Mexico, Germany and India. However, this compilation is presumably incomplete since the German plant at least has sister companies in Belgium (located at Langerbrugge) and in Norway (Fredrikstad) which are not mentioned in the literature.

9.1.2.2. Dioxin formation

The thermal processes which involves carbon and chlorine containing materials and oxygen is suspected in general to be capable of producing dioxins and furans via the so-called “de-novo synthesis”. The process for TiO_2 production described above fits to these conditions; therefore, the carbonaceous dust from the flue gas cleaning was investigated for contamination with PCDD/F.

In four samples taken from different batches dioxin and furan concentrations ranging from 185 to 1100 ng I-TEQ/kg (mainly furans) were found. These values were considerably high compared to the German limit values set in the Ordinance on the Prohibition of Certain Chemicals (the PCDD/F-concentration in one sample in fact exceeded this limit). Thus the question arose whether the plant could be an emission source for airborne dioxins and furans too.

9.1.3. Results and discussion

LUA carried out emission measurements at the main stack of the plant where the flue gas from the thermal afterburner passes through. As the access port for emission testing is located in a short duct between afterburner and stack the measurements faced considerable technical problems, in particular very high flue gas temperatures (> 700 °C). Therefore it was impossible to apply a sampling equipment according to EN 1948. The equipment used was a modified filter/cooler system according to VDI 3499; a bottle filled with 200 ml of ice bath-cooled water was installed in front of the sampling system to cool the gas entering the filter. The sampling probe and the connection tubes were made of quartz glass. At the given port dimensions the sample could only be aspirated transversely to the flue gas flow direction.

As a result, concentrations only in the range of blank values were measured and hence no PCDD/F emission from the stack of the titanium dioxide production plant could be found. Apparently, the waste gas treatment in several steps (dedusting, condensing, washing, desulfurisation, afterburning) sufficiently cleans the flue gas from any PCDD/F which might be released from the chlorination process.

9.1.4. Conclusion

Dioxin emissions to ambient air from the chlorine process for titanium dioxide production as carried out in the investigated plant could not be found. This is probably due to the multi-step waste gas treatment process which catches and/or destroys any formed dioxins. However, some of the waste gas treatment steps were incorporated mainly to allow for an additional production of by-products (carbonaceous fuel, iron chloride, elementary sulphur) which can be sold to the market rather than only for flue gas cleaning. This implies, that similar plants in Europe using the same process for TiO_2-production but not making use of by-products may have different waste gas treatments and hence a different emission situation.

References

1. Ullmann's Encyclopedia of Industrial Chemistry on CD-ROM. Wiley-VCH, Weinheim (1997).

10. Germany

10.1. Case study on “PCDD/F sulphur analogue compounds”

10.1.1. Summary

A plant located in Germany producing sulphur dioxide by combustion of sulphur-containing waste materials (spent sulphuric acid, acidic tars and oils, organic sulphur compounds, miscellaneous coal and coke products) was suspected to cause emissions of PCDD/Fs and possibly their sulphur-analogue compounds polychlorinated dibenzothiophenes (PCDTs) and polychlorinated thianthrenes (PCTAs).

A comprehensive literature survey was conducted therefore with respect to the following questions of:

- Occurrence of PCDTs and PCTAs in environmental matrices
- Toxicological properties of these compounds in comparison to PCDD/Fs
- Information on formation conditions and pathways
- Analytical methods to detect PCDTs and PCTAs

The literature research revealed that data on each of these topics is quite scarce; however, the following statements could be derived:

- Sulphur-analogues of dioxins and furans were found in different environmental compartments; though in most cases only PCDTs were detected.
- The toxicological information is equivocal; some experiments reveal dose-effect relationships similar to those observed with PCDD/Fs, others indicate that sulphur analogue compounds are metabolised much more rapidly and therefore exhibit considerably less toxicity. From precautionary considerations the sulphur analogues should be treated as being of similar toxicological relevance as the PCDD/Fs
- From laboratory experiments, structural considerations and from the observation, that in samples where they could be detected the level of PCDT concentrations appears to be correlated with the level of PCDD/Fs. Similar formation reactions and formation conditions as known for PCDD/Fs may be assumed.

- No validated sampling method is available yet for measurements of the sulphur analogues of dioxins. Thus the methods developed for standard dioxins and furans have to be used (e.g. EN 1948).
- Analytical detection of PCDTs is difficult due to the small mass difference of these compounds compared to the dibenzo-p-dioxins with the same chlorination degree. The mass difference between 1 sulphur atom (PCDTs) and 2 oxygen atoms (PCDDs) is only 0,0177 amu. Hence mass spectrometry with increased resolution (> 18.000) is needed. As no ^{13}C-labelled congener standards are available, only semi-quantitative analysis is possible relating the sulphur analogues to standards of dioxins and furans. Chromatographic separation of PCDTs from PCDFs is poor; improvement seems to be possible by pre-chromatographic derivatisation to the corresponding sulfones.

To evaluate whether such emissions might be possible the company's process was analysed in detail with respect to conditions which may favour a de-novo synthesis of PCDD/Fs and PCDTs/PCTAs. Two process steps were identified which are operated at relevant temperatures between 200 and 900 °C. Hence possible emissions of PCDD/Fs and their sulphur analogue compounds could not be precluded.

Analyses of production residues (coke dust, fly ash and sludge) showed very low PCDD/F concentrations (< 0,1, < 1, and < 10 ng I-TEQ/kg, respectively). Only the sludge sample contained detectable amounts of PCDTs (11 to 42 ng/kg as sum of homologue concentrations).

Further, sampling of stack gases and analyses revealed no significant emissions of PCDD/Fs compared to a blank sample which would correspond to 5 pg I-TEQ/m^3. No sulphur analogue compound could be detected in the flue gases.

10.1.2. Background

The group of polychlorinated dioxins and furans comprises of 210 different chemical compounds. Only 17 of these compounds, being substituted at least in the 2,3,4,7-positions of the ring system, are considered as highly relevant for health effects and thus are analysed and subjected to toxicological assessments (i. e. the assignment of TEFs).

However, besides chlorinated species also other compounds have been under consideration having a similar structure but containing other halogens. Particularly the brominated

PBDD/PBDFs, also comprising 210 different compounds, were focused in the past. For some of these compounds limit values had been introduced in the German Ordinance on the Prohibition of Certain Chemicals.

Furthermore, there is few information on the formation of fluorinated dioxins and furans and much more limited data exist about mixed-halogenated derivatives, which increase the number of potentially hazardous dioxins and furans to more than 5000. Fortunately, the toxic levels as well as environmental persistence of most of these compounds are expected to be much lower than for the polychlorinated dioxins and furans. Therefore, the current practice to restrict analytical efforts to polychlorinated compounds appears to be justified.

But, as also known from some previous investigations, among the polychlorinated compounds with comparable structure there exists another separate group of compounds which may be of importance. These compounds are the so-called “sulphur-analogues” of polychlorinated dioxins and furans, which contain sulphur atoms at the same positions where dioxins and furans have oxygen atoms. While the chemical names “dioxin” and “furan” implicitly indicate the presence of oxygen bridges (see figure 1), the sulphur containing analogues have got completely different names, “thianthrene” for the analogue of dioxin and “thiophene” for the furan-analogue.

Compounds of these groups were found in particular environmental matrices and were subjected to toxicological and analytical research (c.f. sections below). There are also a number of thermal processes involving sulphur containing materials which may be suspected to generate polychlorinated thiophenes and thianthrenes. On the occasion of a case study regarding a facility for SO_2-production located in North Rhine Westphalia a comprehensive review of the current knowledge on these compounds was made which is presented in the following.

10.1.2.1. Description of the sulphur analogue compounds of PCDD and PCDF

If oxygen in polychlorinated dibenzofurans is substituted by sulphur polychlorinated dibenzothiophenes (PCDT) are obtained.

Changing the basic structure of the dibenzodioxin accordingly yields the polychlorinated analogues of the dibenzodioxins, the polychlorinated phenoxathiines and thianthrenes (PCTA) (figure 1).

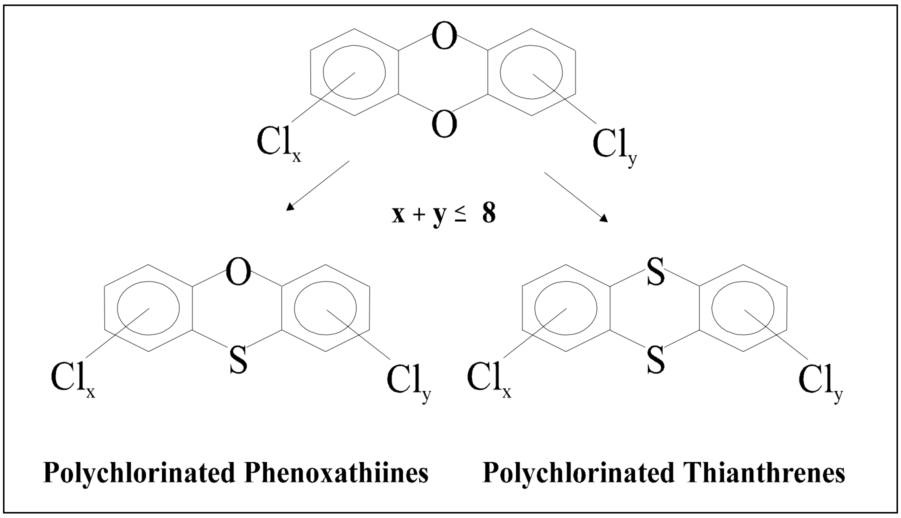

figure 1: polychlorinated dibenzodioxins and sulphur-analogues

The number of theoretically possible congeners corresponds to the number of PCDD and PCDF congeners (75 PCTA, 135 polychlorinated phenoxathiines, 135 PCDT).

In the literature, primarily the polychlorinated dibenzothiophenes (PCDTs) derived from dibenzofurans are mentioned as proof for the presence of sulphur-analogues of the polychlorinated dioxins and furans. Of the dioxin-derived compounds it is reported that the polychlorinated thianthrenes were not detectable at all or in concentrations close to the detection limit of the applied analytical procedure [1] [2] [3, 4].

One path of PCDT formation is the thermal reaction of PCB with elemental sulphur, as has been shown in various laboratory experiments. For example, Aroclor 1254[1] was converted with sulphur, at a temperature of 540°C, to approximately 1 to 2% PCDT (see figure 2). Further reaction products were carbon and hydrogen chloride with remaining unreacted Aroclor 1254. At higher reaction temperatures the PCDT fraction declined [5]. When the PCB compounds used in these experiments were isomers of hexachlorobiphenyl with chlorine substituents in ortho position, tetra-CDTs were preferably formed along with smaller fractions of penta-CDTs. The 3,4,5,3',4',5'-hexachlorobiphenyl with no chlorine in ortho position, however, does not cause formation of tetra-CDT. Therefore, it is assumed that tetra-CDT is formed by exchanging chlorine substituents in ortho position for sulphur which forms the bridge thus closing the ring. Nothing is known about the mechanism of this reaction.

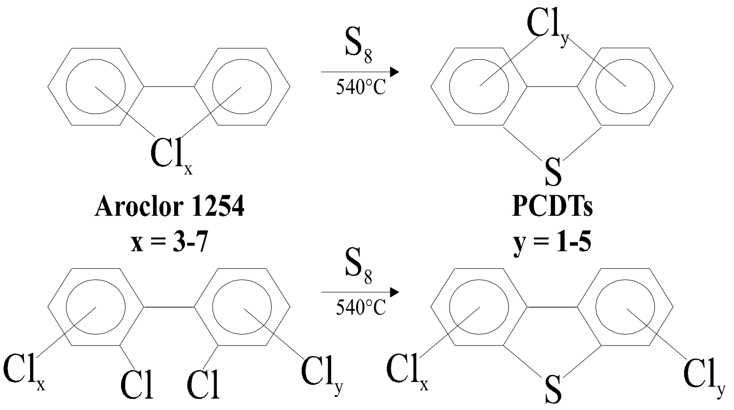

figure 2: possible reaction derived from laboratory experiment

The following possibilities are discussed for the thermal processes:

- Thermal dissociation and recombination of radicals of organic chlorine compounds in the presence of sulphur or sulphur compounds in the combustion zone of combustion processes, but as well in the cooling zone of flue gases. For combustion of car tyres the sulphur fractions present in the vulcanizate as cross-linking agents and chlorine compounds such as chloroprene (2-chloro-1,3-butadiene) may be the initial compounds.
- Direct chlorination of the sulphur analogues of the dibenzofurans (dibenzothiophenes) or dibenzodioxins (phenoxathiines and thianthrenes). This possibility requires the presence of not chlorinated compounds as precursors. In fact, such precursors were detected in fuel and diesel oils and, as it is known, sulphur-containing fuel oil is added in the start-up phase of thermal combustion processes. Comparing normal operation phase without addition of sulphur-containing fuel oil and the start-up phase with addition of sulphur-containing fuel oil no significant difference in the rate of formation of measured PCDTs is observed [6].

---

[1] Trading name of a mixture of PCBs, main components are tri-, tetra-, penta- und hexachlorobiphenyls

10.1.2.2. Occurrence in the environment

Traces of polychlorinated dibenzothiophenes were found in emissions of high temperature metallurgical processes [3] [4] [7], garbage incinerators and in traffic-related road dust. [6, 8, 9]. Moreover, PCDTs were identified in waste water discharged by the pulp and paper industry (in sediments and aquatic organisms) [10].

Polychlorinated thianthrenes (2,3,7,8-Cl_4-thianthrene) were detected in the sediment of a sewer coming from a chemical plant in Niagara Falls, USA [1]. However, these compounds were produced in that plant and entry was confined to that location.

Octachlorothianthrene was found by *Hagenmaier et al* [2]. *(1992)* in sewage sludge.

Polychlorinated dibenzothiophenes (PCDTs) such as 2,3,7,8-tetra-CDT were detected in the waste gas and fly ash of garbage incinerators and in residues from an arc furnace of a car metal reclamation plant and an aluminium smelting plant [7, 11]. The concentrations of PCDTs were consistently higher in the ash samples than in the gas samples [4] with the concentrations of the tetra-CDTs frequently reaching the levels of the tetra-CDDs [4]. The ash samples were taken from electrostatic precipitators. For formation of these trace substances a temperature range of 300 to 850°C is suggested. Studies of gas samples taken ahead of and after the electrostatic precipitator in an aluminium smelting plant yielded different distributions of the isomers of tetra-CDT. This shows that the isomers of tetra-CDT have different adsorption properties. Contrary to this, the tri-CDT isomers showed no differences [4]. There is evidence that PCDTs are also formed during the combustion of car tyres. It is not surprising to find sulphur analogues in sewage sludge in addition to dioxins and furans, because the waste water treatment process causes PCBs to accumulate in sewage sludge and elemental sulphur may develop in the anaerobic biological decomposition process as reagent.

Studied to date the sulphur analogues of dioxins and furans were always found in conjunction with dioxins and furans (PCDDs/PCDFs). In fly ash samples of garbage incinerators the fraction of sulphur analogues of furans (PCDTs) was consistently higher than that of PCDDs and lower than that of PCDFs.

As results of studies on crayfish, lobsters and worms in Sweden [5], on crabs caught off the coast of Newark [12] and on pine needles show, PCDTs are widely spread in the environment [13].

The existing literature does not provide any evidence of the occurrence of polychlorinated phenoxathiines in environmental samples.

10.1.2.3. Measurement of the S-analogues of dioxins

10.1.2.3.1. Sampling

No validated method for waste gas sampling of sulphur analogues of the dioxins is available. However, contrary to the development of sampling methods for PCDDs and PCDFs, which took many years to reach a sufficient reliability, there is a lot of experience to draw on nowadays. In spite of that, the efforts necessary to adjust and validate the methods for PCDDs and PCDFs to the sampling of PCDTs and PCTAs should not be underestimated.

Even after many years of development the existing sampling methods for measuring the PCDD and PCDF emissions have a barely acceptable standard deviation. In the case of PCDD/F sampling, relatively well-known units for dust collection and absorption or adsorption are combined. Moreover, ^{13}C-labelled standards are available which allow to study the behaviour and properties of various components of the sampling equipment and which can be added as reference material for sampling.

Such standards do not exist for the PCDTs and PCTAs. In addition, it is unknown, for example, how PCDTs and PCTAs behave at higher temperatures on a dust filter or how they are retained in various compartments. In the case of PCDDs and PCDFs, a number of scientific studies on sampling procedures were necessary to make sure that thermally or chemically catalyst-promoted changes remained of secondary importance during sampling of the substances to be measured while maintaining certain boundary conditions. This is important in order to permit standardisation of sampling systems according to CEN1948, 1-3, as reference methods.

The application of PCDD and PCDF sampling procedures to the sampling of the chemically less stable sulphur analogues, the PCDTs and PCTAs, appears risky, because to low concentrations cannot be quantified.

However, it is recommendable to accept this risk if measurements become necessary, because a validation of a sampling procedure for the sulphur analogues along the lines of the CEN standardisation of sampling PCDDs and PCDFs requires ^{13}C-labelled standards and therefore it cannot be satisfactorily realised within a short period of time.

Under these circumstances the evaluation of the measured values of PCDTs and PCTAs needs to take into account the lower quality in comparison to the results of measurements of PCDDs and PCDFs.

10.1.2.3.2. Analysis

Preparation of the samples for the analysis of sulphur analogues of dioxins and furans follows the procedure used in the case of PCDDs and PCDFs. Elution of PCDTs on a non-polar chromatographic column (SE-54) depends on the number of chlorine atoms — the higher the degree of chlorination the longer is the retention time on the column. To counter this effect a higher elution temperature is required. PCDTs have a higher retention time (higher elution temperature) than comparable PCDDs. They are eluted in the range of the next higher homologous series compared to the PCDDs (i.e., tetra-CDTs elute in the range of penta-CDDs).

Mass overlap makes it difficult to analyse PCDTs in the presence of PCDDs. The exact mass of the molecular ion M^+ of PCDTs is very close to that of PCDDs with the difference amounting to only 0,0177 mass units (Example: TCDDs 319,8965 - TCDTs 319,8788). Separation of masses with this mass difference requires a high-resolution mass spectrometer with a resolution of ($R = M/\Delta M$) of 18.000 - 26.000 for tetra- to octachloro-compounds. This resolution is considerably higher than needed for routine measurements of PCDDs and PCDFs in environmental samples (5 - 10.000).

Sielex und Andersson (1997) [14] reported on the overlapping retention times of PCDTs with those of PCDDs on many chromatographic columns and recognised the fact that the structurally similar heterocyclic oxygen and sulphur compounds cannot be separated by the conventional clean-up procedures.

Buser [5] used in 1991 for the analytical determination a double focusing magnetic field sector hybrid mass spectrometer in the EI (electric ionisation) as well as in the NCI (negative ion capture) mode.

Defined standard substances are not available for any of the procedures.

Tetrachlorodibenzothiophenes are formed by thermal reaction of hexachlorobiphenyls with sulphur at 540°C. Mono- to penta-, and tri- to hepta-CDTs are obtained by thermal reaction of commercial PCB (Aroclor) with sulphur. All reactions have in common that mixtures with different degrees of chlorination arise.

However, no congener-specific reference materials neither the native congeners nor the $^{13}C_{12}$-labelled congeners, are commercially available. All studies to date were confined to the qualitative determination of sulphur analogous dioxins and furanes along with the determination of PCDDs and PCDFs, to semi-quantitative estimates of the concentrations in relation to the concentrations of PCDDs and PCDFs or in relation to a $^{13}C_{12}$-2,3,7,8-TCDD congener which was added as internal standard.

A congener-specific analysis of sulphur analogues of dioxins and furans is impossible at this time, because there are no suitable standards which are free of congeners and a chromatographic separation of the various congeners is impossible, too.

In summary it can be said about measurement of sulphur analogous dioxins:

- in a first step the sampling method developed for PCDDs and PCDFs according to CEN 1948 Part 1-3 can be carried out, at possibly non quantifiable quality losses;
- according to the literature the sulphur analogous homologues of the tri-, tetra-, and pentachlorodibenzothiophenes can be qualitatively detected in presence of PCDDs and PCDFs provided that the required equipment is available (HRGC/HRMS);
- a semi-quantitative estimate of the homologues of sulphur analogous dioxins and furans in relation to present PCDDs and PCDFs is possible;
- a quantitative analysis of the individual congeners is impossible at present because they cannot be chromatographically separated and suitable standards are not available;
- with the procedures of clean-up, chromatographic separation and HR/MS determination (with resolutions of 5.000 - 10.000) usually applied to chlorinated dioxins and furans the sulphur analogues cannot be separated from the PCDDs and PCDFs but are included in the signals of the homologues;

- expensive and sophisticated (HRGC/HRMS) equipment and analytical separation and clean-up procedures are necessary to detect the PCDTs in presence of PCDDs and PCDFs because of their chemical similarity;
- no gas chromatographic separation can be achieved with the available analytical procedures because of similar polar properties and hardly different retention times. Routine studies using SIMS yielded undifferentiated mass spectra because of the small differences in the molecular masses. The use of electric ionisation (EI) led to complicated decay patterns caused by fragmentation of the molecular ions present in the SIMS spectra which complicated the evaluation. A recently described method appears promising. According to this method PCDTs present in a mixture of PCDDs and PCDFs are converted to the corresponding sulphones and separated by GC. It was shown that this method of sample preparation can be combined with the routinely used measurements.

10.1.2.4. Toxicological evaluation of the sulphur analogues of dioxins and furans

The sulphur analogous dioxins and furans are compounds which are related to dioxins and furans. Therefore, their mechanism of effect corresponds to that of dioxins and furans. They belong to compounds which possess a potential of negatively affecting the Ah receptor-mediated mechanism; therefore, in the literature, there is discussion of a toxicity which is typical of dioxins. [4, 15].

10.1.2.5. Mechanism of effect

According to the present model of effects, the sulphur analogues of dioxins and furans affect the molecular level, like dioxins and furans, by initially binding to the cytosolic Ah receptor. The forming complex is attached to so-called „dioxin responsive elements“ of the DNA and causes the expression of various genes. Subsequently, the transcribed mRNA entered into the cytosol of the cell induces the synthesis of protein and various cytochrome P450-dependent monooxygenases. This triggers a multitude of further biochemical responses which are of the same rank but depend on the species and the potency of induction.

The induction of specific cytochrome P450 enzymes (CYP1A1 and CYP1A2; former nomenclature P4501A1 and P4501A2) is one of the most sensitive biochemical responses. The level of response is expressed by the activities of the aryl hydrocarbon hydroxylase

(AHH) and/or 7-ethoxyresorufin O-deethylase (EROD) which are measured. [16] Studies of Sprague-Dawley rats to determine the importance of the Ah receptor for the toxicity of polyhalogenated aryl hydrocarbons have shown, that the induction of the enzymes CYP1A1 and CYP1A2, which metabolise foreign substances, by TCDD is of no importance to tumour promotion. Further experiments with C57BL/6J mice have also shown that induction of these two enzymes does not play any role in the acute toxicity of TCDD. In spite of the lack of any correlation of the Ah receptor-mediated induction of CYP1A1 and CYP1A2 with the toxicity of TCDD, the measurement of the induction of CYP1A1 and CYP1A2 remains the most sensitive method of detecting TCDD and related compounds in biological matter, even though most of the toxic effects appear at doses which are higher than those needed for enzyme induction [17].

A number of effects, however, cannot be solely explained by binding to the Ah receptor [17-19].

Haper et. al. [20]conducted studies with C57BL/6 and DBA/2 mice which showed that for the most toxic congeners of PCDDs, PCDFs and PCBs the immunotoxic response is a more sensitive indicator than CYP1A1 induction. [16, 20]. But not all published findings on the effects of TCDD in the low-dose range on the immune system turned out to be reproducible [19].

10.1.2.6. Studies of the induction of cytochrome P450, CYP

Good agreement between toxic potency and induction of CYP1A1 expressed by the measured AHH or EROD activity was obtained mainly for 2,3,7,8-substituted PCDD and PCDF congeners. The potency of enzyme induction of individual dioxins and furans (measured EROD or AHH activity in vitro) agreed largely with the potency of causing effects such as, for example, weight loss and thymus atrophy.[17] This correlation justifies the use of enzyme induction in vitro as a measure of dioxin-like toxic potency. The fact that many known and possibly also unknown compounds may cause dioxin-like toxicity and the difficulty to analyse them chemically led to the development of a bioassay (EROD induction in H-4IIE cells = rat liver cell line). With the help of the EROD induction potency the toxicity equivalent TEQ can be calculated [15, 16, 21].

10.1.2.7. In vitro studies

Studies of the CYP1A1 induction potency of the sulphur analogues 2,3,7,8-tetrachlorothianthrene (TCTA) and 2,3,7,8-tetrachlorodibenzothiophene (TCDT) as well as of TCDD in mice liver cell cultures Hepa-1 revealed marked differences in the induction potency between the two sulphur analogues and also between the sulphur analogues and TCDD. From these differences it can be concluded that substituting the oxygen atom for a sulphur atom strongly reduces the potency to induce AHH/EROD activities.

The relative potency of PCDTs in a H4IIE sample is similar to that of PCDDs (the toxicity equivalent factor TEF for a synthetic mixture of PCDTs is 0,00425) [15, 16, 22].

10.1.2.8. Study of the toxicity of TCTA in animal experiments

The oral intake of differently high doses of TCTA and, for comparison, of TCDD, led in Wistar rats at high TCTA doses to a significant reduction of the rate increase of body weight and of the weight of thymus and spleen and increased the microsomal CYP content in the liver as well as the EROD activity in male Wistar rats. The NOAEL was found to be for TCTA 1µg/(kg * 14 days) and for TCDD in female rats 0,001µg/(kg * day). This study shows that TCTA is less toxic to rats than TCDD [17, 23, 24].

A subchronic study with NMRI mice in which doses were used which corresponded to the lethal TCDD doses in mice yielded no evidence of a weight loss or other obvious signs of toxicity [22].

10.1.2.9. Special toxicity

One experiment with viable cells showed that TCTA is only slightly cytotoxic [16].

10.1.2.10. Kinetics of elimination

The kinetics of elimination and the toxicity of 2,3,7,8-tetrachlorothianthrene were studied with NMRI mice and with mice liver homogenate. The rate of metabolisation of TCTA in mice liver homogenate was comparable to that of PCDDs not substituted at the 2,3,7,8 positions, while TCDD and 2,3,7,8,-TCDF do not metabolise within such short time (4 hours) under comparable conditions. TCTA is rapidly removed from the liver and the entire body.

The studies performed with NMRI mice yielded a much lower half-life of 1 day for TCTA in male NMRI mice as compared to TCDD which had a half life of 8,5 to 24 days [22].

10.1.2.11. Studies of accumulation

R. J. Pruell et al. [25] performed a laboratory experiment to measure accumulation of selected polychlorinated compounds in sandworms, crabs and venus clams from sediments in the Passaic River, New Jersey.

All three species accumulated 2,3,7,8-tetrachlorodibenzo-p-dioxin, 2,3,7,8-tetrachlorodibenzofuran, polychlorinated biphenyls and the sulphur analogue 2,4,6,8-tetrachlorodibenzothiophene.

In order to compare the results between species and compounds, accumulation factors were calculated. Generally higher accumulation factors (AFs) were obtained for crabs and venus clams while they were lower for sandworms. However, the AFs for 2,4,6,8-TCDT were significantly higher for crabs than for sandworms and venus clams. This may be due to different metabolisation or to a species dependent composition of adipose tissue which leads to a different accumulation in the tissue [25].

10.1.2.12. Summary of toxicological evaluation

There are only few studies on the sulphur analogues of PCDDs and PCDFs. The in vitro studies provide evidence that the potency of induction of Ah receptor-mediated processes typical for dioxins is lower than that of PCDDs and PCDFs. The calculation of toxicity equivalent factors (TEFs) based on the measurement of the enzyme induction potency in the bioassay yielded lower TEFs for the sulphur analogues than for dioxins and furans. In vivo studies are available only for TCTA. These studies with rats and mice show that the toxic effect of TCTA is lower than that of TCDD in rats as well as in mice.

Although the results of the studies on the subchronic toxicity and the results from the in vitro studies of the toxicity provide evidence that replacement of an oxygen atom by a sulphur atom measurably reduces the toxicity of the compound, the results of in vivo studies on kinetics of elimination speak against the application of the TEF to the sulphur analogues of the dioxins for evaluation. According to these studies the rapid metabolic elimination of the compound in the liver appears to be the main factor in preventing or reducing toxic effects. Whether at all and to what extent the rapid kinetics of elimination apply to humans, in vivo and in vitro, remains unclear.

10.1.3. Case study: Sulphur analogues of dioxins in a plant for production of SO2 from sulphur-containing waste materials

10.1.3.1. Process description

In a rotary kiln sulphur containing waste material is thermally decomposed to produce SO_2. Spent sulphuric acids, sulphur-containing tars, sulphur-containing activated carbon as well as acidic tars and resins are thermally degraded to SO_2, CO_2 and H_2O in the investigated installation with adjoining intermediate and afterburning chambers. With regard to the chemical structure, the input material belongs to the aliphatic, alicyclic, heterocyclic and aromatic compounds including their halogenated derivatives such as PCBs. Inside the rotating cylinder reducing conditions are maintained which means that the organic carbon fraction is coked. Complete combustion is achieved in the adjoining afterburning chambers to which additional air is supplied.

In the following the process steps for SO_2 production including flue gas treatment are discussed taking into consideration the temperature range at which these steps occur in normal operation:

- **Thermal decomposition (900°C - 1050°C)**

In the rotary kiln a temperature between 900°C and 1050°C is maintained in a bed of coke. The waste products such as the spent sulphuric acids and acidic tar mixtures are added together with sulphur to achieve the desired SO_2 concentration. The amount of heat is produced by combustion and coking of the organic fractions of acidic tars and resins and by combustion of waste oil and sulphur. Underfeed primary air and oxygen are injected into the furnace to support this process. In the reducing atmosphere of the rotary kiln fractions of the organic carbon in the input material are coked. Coke dust is produced which is continuously removed from the kiln at 850°C, indirectly cooled by circulating cooling water and than wetted.

- **Thermal afterburning (1050°C - 1300°C)**

The flue gas leaves the rotary kiln and enters the intermediate chamber where secondary air or oxygen is injected. It passes then through two afterburning chambers. It takes the flue gas more than 5 seconds to pass the intermediate chamber, the first afterburning chamber and the second afterburning chamber. During that time a temperature level of approx. 1200 to 1300°C is reached. Ash which is not carried off in the coke dust is entrained in the flue gas flow from the furnace and brought to the adjoining afterburning chambers where pasty, glutinous slag is formed. The fluid hot slag is withdrawn in regular intervals. Residual slag remaining on the refractory lining of the afterburning chambers is removed during times the plant is shut down.

- **Flue gas cooling (1200°C - 300°C)**

After passing the intermediate chamber and two afterburning chambers the flue gas flow is cooled down in the waste heat boiler from 1200°C to 300°C. The waste heat is used to produce superheated steam of 450°C at 40 bar and saturated steam of 240°C at 40 bar. The ash particles not deposited in the afterburning chambers settle on the heat exchanger pipes of the superheater and evaporator. These deposits need to be removed in regular intervals.

- **Flue gas cleaning (300°C - 35°C)**

The flue gas is drawn off after leaving the waste heat boiler via a hot air blower and passing a two-stage scrubber and a single-stage wet electrostatic gas cleaning unit for further cooling and cleaning. As scrubbing fluid sulphuric acid (70%) is circulated to remove dust, mercury and halogens. Residual fly ash which passed the waste heat boiler is collected in the scrubbers and finally in the electrostatic precipitator. It is returned to the rotary kiln as acidic sludge left from the gas cleaning processes. The flue gas which has been cooled to temperatures between 35°C and 50°C is passed to the SO_2 absorption unit.

- **SO_2 absorption (30°C - 40°C)**

The SO_2 in the flue gas is removed by counterflow scrubbing with an aqueous solution of an organic dicarbonic acid which is buffered with sodium lye. In a subsequent two-stage final collector the remaining SO_2 is reduced to less than 50 mg/m³ in the first stage by sodium lye injection and the remaining Hg is reduced to less than 50 µg/m³ in the second stage by adding sodium peroxide sulphate .

- **Absorbent treatment (20°C - 50°C)**

From the absorption of SO_2, soluble sulphur containing reaction products remain which need to be withdrawn from the absorption cycle. This is achieved by acidification of these residues with sulphuric acid in a boiling process to which — among other things — a solution of sodium sulphite from the SO_2 absorption unit is added. Thus sodium sulphate is formed which is re-crystallised to obtain Glauber's salt ($Na_2SO_4 \cdot 10\ H_2O$).

- **SO_2 desorption (100°C - 25°C)**

In the desorber SO_2 in the absorbent is removed with water vapour at 100°C. Above the desorber a 50% mixture of SO_2 and H_2O is drawn off and cooled to between 25°C and 30°C.

- **SO_2 drying, concentration/condensation (25°C - 30°C)**

Finally, SO_2 is dried to a residual water vapour content of 50 ppm at 25°C to 30°C with sulphuric acid (78%) as drying agent in a two-stage drying process with acid circulation and condensation at a pressure of 5 bar and a temperature of 28°C.

10.1.3.2. Possible formation paths

According to present knowledge the sulphur analogues of dioxins and furans always occur in conjunction with dioxins and furans. This allows an assumption of similar preconditions for the formation of these two groups of compounds. Therefore, it no surprise that the pathways of their thermal formation run in parallel. The comparison of the formation of PCDTs from PCBs in presence of elemental sulphur derived in the laboratory (see figure 3) with the familiar ring formation and conversion of 3,3',4,4'-tetrachlorobiphenyl to 2,3,7,8-tetrachlorodibenzofuran is shown in the following figures (figure 4: example of a ring forming reaction):

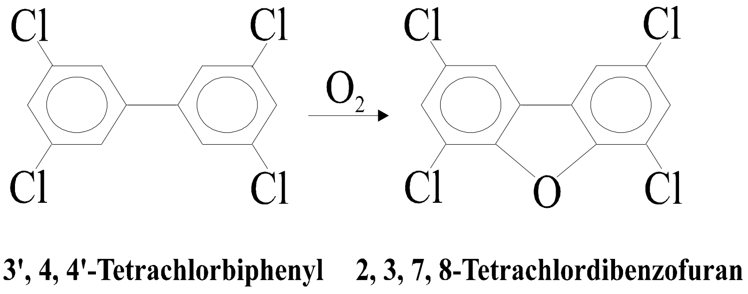

figure 3: Example of familiar ring forming reaction

The mechanism is a radical reaction. Such types of reactions occur in (uncontrolled) fires and combustion processes above 350°C. In a similar way, the ring forming reaction of 3,3',4,4'-tetrachlorodiphenylether produces the well-known „Seveso dioxin“ 2,3,7,8-tetrachlorodibenzo-p-dioxin.

Chlorination of the sulphur analogues of dibenzofurans (dibenzothiophenes) or dioxins (phenoxathiines and thianthrenes) is comparable to the formation of dioxins and furans which has become known as substituent reaction, as the following example of the formation of 2,3,7,8-tetrachlorodibenzo-p-dioxin shows.

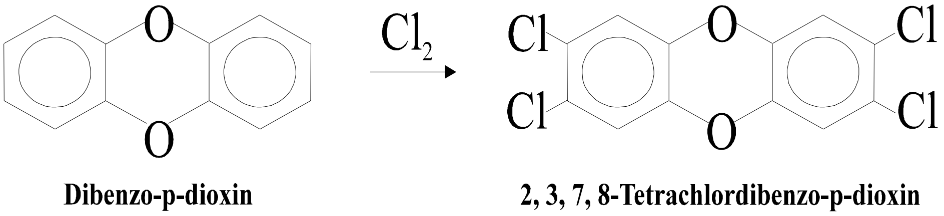

figure 4: Example of a substituent reaction

10.1.3.3. Possible formation sites

From process description the removal of coke dust at 850°C from the thermal decomposition process and flue gas cooling at temperatures of ≥ 300°C appear as the likely sites of formation for which temperatures between 300 and 850°C are required

10.1.4. Results and discussion

10.1.4.1. Measurements

10.1.4.1.1. PCDD/Fs and sulphur analogues in production residues

In order to evaluate the potential for the formation of PCDD/F and their sulphur analogues residues from different production steps were sampled and analysed. Three samples each were taken from the:

- coke dust produced during the thermal decomposition of input materials
- fly ash deposited in and removed from flue gas cooling
- sludge from the first scrubber of the waste gas cleaning system.

All samples were analysed for PCDD/F at the LUA laboratory and at an external laboratory which in addition was capable to determine the concentrations of sulphur analogues. This was achieved after conventional PCDD/F cleanup by HRGC/HRMS analysis with a resolution of 10.000 amu. Calculation was done using the internal ^{13}C standards for PCDD/F and with use of a response factor measured for native tetrachlorodibenzothiophene. The following results were obtained (see table 1):

	Coke dust	Fly ash	Sludge	Detection Limit [ng/kg]
PCDD/F [ng I-TEQ/kg] *)	0,01 / 0,2	0,043 / < 0,7	2,7 / 8,2	
Sum PCDF [ng/kg]	3 / 5,5	2,3 / 1,4	111 / 216	
Sum PCDD [ng/kg]	4,6 / n.d.	2,7 / 6,5	26 / 35,9	
PCD-Thiophens $^{+}$)				
- Sum TetraCDT [ng/kg]	n.d.	n.d.	37	1
- Sum PentaCDT [ng/kg]	n.d.	n.d.	42	2
- Sum HexaCDT [ng/kg]	n.d.	n.d.	25	2
- Sum HeptaCDT [ng/kg]	n.d.	n.d.	11	3
- OctaCDT [ng/kg]	n.d.	n.d.	n.d.	5
PCD-Thianthrenes $^{+)}$				
- Sum TetraCTA [ng/kg]	n.d.	n.d.	n.d.	2
- Sum PentaCTA [ng/kg]	n.d.	n.d.	n.d.	3
- Sum HexaCTA [ng/kg]	n.d.	n.d.	n.d.	4
- Sum HeptaCTA [ng/kg]	n.d.	n.d.	n.d.	6
- OctaCTA [ng/kg]	n.d.	n.d.	n.d.	8

table 1 : Contamination of production residues with polychlorinated dioxins and furans and their sulphur analogues; n.d.: not detectable; *) first value LUA, second external laboratory; +) only analysed by external laboratory

The results consistently show very low concentrations for all measured compounds in the three samples. With respect to these low concentrations the results regarding dioxins and furans obtained by the two laboratories compare well. Only the sludge sample appeared to contain traces of polychlorinated thiophens, whereas polychlorinated thianthrenes could not be detected at all.

Having in mind that separation of PCDT from PCDD/F is difficult due to the small mass difference between thiophens and dioxins all samples were analysed again according to the method of Sielex and Andersson [14] which makes use of an oxidation step converting the sulphur analogues to their corresponding sulphones. In contrast to the results shown in table 1 no significant concentrations of PCDTs were found in any of the samples (with detection limits in the range of 10 ng/kg for PCDTs and 20 ng/kg for the corresponding sulphones).

10.1.4.1.2. PCDD/Fs and sulphur analogues in stack emission

Although the analyses of production residues had not revealed a considerable contamination with PCDD/Fs or their sulphur analogue compounds the flue gas emissions were investigated additionally for precautionary reasons.

Before entering ambient air the flue gas (combined from both rotary kilns) passes a cooler/gas washing facility combined with an electrostatic precipitator, the SO_2-absorption stage, an alkaline gas washing unit and a mercury absorber.

Sampling was carried out on three days in March 2000; the sampling point was located at a horizontal duct which connects the final gas cleaning stage with the stack. On the first and third day both kilns operated at full load during the sampling period; after a short-time shut-down the start-up phase of kiln one was included in the sampling period on the second day.

PCDD/F sampling was done according to EN 1948 with a cooled sampling probe; flue gas conditions (flow velocity, temperatures) were determined on 2 lines with six points per line prior to installing the dioxin sampling apparatus. Due to spatial restrictions the sampling probe could not be shifted and therefore sampling was done at one sampling position only. Isokinetic conditions were maintained by regulation of the sampling flow rate on the basis of continuous measurement of dynamic pressure and temperature in the stack.

As no specific sampling method for the sulphur analogue compounds (PCDT, PCTA) is known, the samples obtained with the PCDD/F sampling method were analysed for both classes of compounds. The analyses were carried out by an external laboratory which beyond its routine PCDD/F analysis (performed according to EN 1948) has also experience in analysing PCDT and PCTA homologues.

The following results were obtained:

pg/m³	Sample 1	Sample 2	Sample 3	Field blank
PCDD/Fs				
I-TEQ	0,6	0,3	0,3	0,5
I-TEQ max (incl. LoD)*)	1,6	1,3	1,3	1,5
ΣPCDD	46	39	46	10
ΣPCDF	36	16	17	37
PCDTs	Not detectable at LoDs from 2-30 pg/m³			
PCTAs	Not detectable at LoDs from 3-30 pg/m³			

table 2 Synopsis of the results of stack gas analyses
LoD: limit of detection (analytical)
***) analytical LoDs for all non-detected congeners (signal to noise level < 3) included**

As revealed by the results presented in table 2 only traces of PCDD/Fs could be found in the stack gases; however, the concentration in the stack gas samples was not significantly different from the field blank. No indication was obtained at all for the presence of sulphur analogue compounds; even if they were present, due to the given analytical limits of detection, their maximum concentrations (sum of all homologues) would have been 64 and 68 pg/m³ for PCDTs and PCTAs respectively. The same, however, applies for the field blank sample; hence, it can be concluded that no sulphur analogue dioxins and furans are emitted to ambient air by the investigated plant.

The emissions of PCDD/Fs are well below the current emission limit of 100 pg I-TEQ/m³ set for hazardous waste incinerators in Europe which in Germany also is valid for all waste combustion or co-combustion plants.

10.1.5. Conclusion

The current knowledge on sulphur analogue compounds of the standard PCDD/Fs appears to be very limited. Not much is known about the toxicological relevance of this group of compounds. As long as no better data is available they should be considered as equally toxic as PCDD/Fs for precautionary reasons. Methods of analysis have been developed by few research groups hence these groups also provide all data available so far on the occurrence of these compounds in environmental matrices. Following this information, particularly PCDT could be found in waste gases and fly ash of some thermal processes as well as in sewage sludge. Their concentrations usually were lower than the always accompanying PCDD/Fs; however, particular PCDT congeners occasionally reached PCDD/F levels.

On this background it appears reasonable to assume that thermal processes involving agents and chemicals needed for the formation of PCDTs and PCTAs may cause emissions of these compounds via production residues and flue gases.

However, the case study carried out at a sulphur dioxide producing plant revealed that this plant did not emit any relevant amounts of PCDD/Fs and their sulphur analogue compounds. A reason for this result could possibly be found in the high SO_2 generation rate for which the production process is optimised for. In waste incineration SO_2 previously has been identified to act as an inhibiting agent for PCDD/F formation [26].

It should be noted that the obtained results are valid only for the investigated plant and may not be applied generally.

References

1. D. R. Hilker, K. M. Aldous, R. M. Smith, P. W. O'Keefe, J. F. Gierthy, J. Jurusik, S. W. Hibbins, D. Spink and R. J. Parillo, Detection of Sulfur Analog of 2,3,7,8-TCDD in the Environment, *Chemosphere* **14**, 1275-1284 (1985).
2. H. Hagenmaier, J. She, T. Benz, N. Dawidowski, L. Düsterhöft and C. Lindig, Analysis of sewage sludge for polyhalogenated Dibenzo-p-Dioxins, Dibenzofurans and Diphenylethers, *Chemosphere* **25**, 1457-1462 (1992).
3. S. Sinkkonen, E. Kolehmainen, J. Koistinen and M. Lahtiperä, High-resolution gas chromatographic-mass spectrometric determination of neutral chlorinated aromatic sulphur compounds in stack gas samples, *Journal of Chromatography* **641**, 309-317 (1993).
4. S. Sinkkonen, A. Vattulainen, J.-P. Aittola, J. Paasivirta, J. Tarhanen and M. Lahtiperä, Metal Reclamation Produces sulfphur Analogues of Toxic Dioxins and Furans, *Chemosphere* **28**, 1279- 1288 (1994).
5. H. R. Buser and C. Rappe, Determination of Polychlorodibenzothiophenes, the sulfur analogues of Polychlorodibenzofurans, Using Various Gas Chromatopraphic/Mass Spectrometric Techniques, *Anal. Chem.* **63**, 1210-1217 (1991).
6. H.-R. Buser, I. S. Dolezal, M. Wolfensberger and C. Rappe, Polychlorodibenzothiophenes, the Sulfur Analogues of the Polychlorodibenzofurans Identified in Incineration Samples, *Environmental Science & Technology* **25**, 1637-1643 (1991).
7. H. R. Buser, Identification and Sources of Dioxin-Like Compounds: I. Polychlorodibenzothiophenes and Polychlorothianthrenes, The Sulfur-Analogues of the Polychlorodibenzofurans and Polychlorodibenzodioxins, *Chemosphere* **25**, 45-48 (1992).
8. U. Riehle, Analytik der polyhalogenierten (Brom/Chlor)-Dibenzodioxine und Dibenzofurane und deren thermische Bildung in einem Verbrennungsmotor, Ph.D. Thesis, Universität Ulm.
9. S. Sinkkonen, PCDTs in the environment, *Chemosphere,* pp. 2585-2594 (1997).
10. S. L. Huntley, R. J. Wenninger, D. J. Paustenboch, A. S. Wong and W. J. Luksemburg, Potential source of polychlorinated dibenzothiophenes in the Passaic River, New Jersey, *Chemosphere* **29**, 257-272 (1994).
11. J. P. Aittola, J. Paasivirta, A. Vattulainen, S. Sinkkonen, J. Koistinen and J. Tarhanen, Formation of Chloroaromatics at a Metal Reclamation Plant and Efficiency of Stack Filter in their Removal from Emission, *Chemosphere* **32**, 99-108 (1996).
12. Z. Cai, D. E. Giblin, V. M. S. Ramanujam, M. L. Gross and A. Cristini, Mass-profile monitoring in trace analysis: Identification of polychlorodibenzothiophenes in crab tissues collected from the Newark/Raritan Bay system, *Environ. Sci. Technol.* **28**, 1535-1538 (1994).
13. S. Sinkkonen, T. Rantio, A. Vattulainen, J.-P. Aittola, J. Paasivirta and M. Lahtiperä, Chlorohydrocarbons, PCB congeners, polychlorodioxins, furans and

dibenzothiophenes in pine needles in the vicinity of a metal reclamation plant, *Chemosphere* **30**, 2227-2239 (1995).

14. K. Sielex and J. T. Andersson, Separation of polychlorinated dibenzothiophenes from polychlorinated dibenzodioxins and -furans, *Fresenius J. Anal. Chem.* **359**, 261- 266 (1997).

15. J. P.Giesy, J. p. Ludwig and D. E. Tillit, Dioxins, Dibenzofurans, PCB`s and Colonial, Fish-Eating Water Birds; Edited by][µg I-TEQ/t] Arnold Schecter), *Dioxins and Health* ., Plenum Press (1994).

16. P. Kopponen, S. Sinkkonen, A. Poso, J. Gynther and S. Kärenlampi, Sulfur Analogues of Polychlorinated Dibentz-p-Dioxins, Dibenzofurans and Diphenyl Ethers as Inducers of CYP1A1 in Mouse Hepatoma Cell Culture and Structure-Activity Relationships, *Environmental Toxicology and Chemistry* **13**, 1543-1548 (1994).

17. P. Cikryt, Dioxine: Wirkungsmechanismen und Risiken, *Nachr. Chem. Tech. Lab.* **39** (1991).

18. H. Marquardt and S. G. Schäfer, Lehrbuch der Toxikologie,, BI-Wiss.-Verlag (1994).

19. *Dioxin-Information und EPA-Reassessment, Organohalogen Compounds* **22**, p. 121 ff (1995).

20. N. Haper, K. Connor and S. Safe, Immunotoxic potencies of polychlorinated biphenyl (PCB, dibenzofuran (PCDF) and dibenzo-p-dioxin (PCDD congeners in C57BL/6 and DBA/2 mice, *Toxicology* **80**, 217-227 (1993).

21. A. Hanberg, M. Stahlberg, A. Georgellis, C. d. Wit and U. G. Ahlborg, Swedish Dioxin Survey: Evaluation of the H-4-II E Bioassay for Screening Environmenteal Samples for Dioxin-like Enzyme Induction, *Pharmacology & Toxicology* **69**, 442-449 (1991).

22. R. Weber, H. Hagenmaier and D. Schrenk, Elimination Kinetics and Toxicity of 2,3,7,8-Tetrachlorothianthren, a Thio Analogue of 2,3,7,8-TCDD, *Chemosphere* **36**, 2635-2641 (1998).

23. J. R. Olson, H. L. Tai, B. P. McGarrigle, T. R. Barfknecht and L. W. Smith, Assessing dioxin-like activity of chlorinated thianthrenes, *Abstracts, 30th Annual Meeting, Society of Toxicology, Dallas, TX, February* **11**, 264.

24. R. E. Peterson, H. M. Theobald and G. L. Kimmel, Developmental and Reproductive Toxicity of Dioxins and Related Compounds: Cross-Species Comparisons, *Critical Reviews in Toxicology* **23**, 283-335 (1993).

25. R. J. Pruell, N. I. Rubinstein, B. K. Taplin, J. A. LiVolsi and D. B. R., Accumulation of Polychlorinated Organic Contaminants from Sediment by Three Benthic Marine Species, *Arch. Environ. Contam.*

26. D. Griffin, A new theory of dioxin formation in municipal solid waste incineration, *Chemosphere* **15**, 1987-1990 (1986).

11. Germany

11.1. Dioxin emissions from Diesel Engines

11.1.1. Preface

This part of the report was originally released within the interim progress report submitted to DG Environment covering the year 1997. As this report was not made public it was decided to include the work on diesel engine emissions into the Stage II report.

11.1.2. Summary

PCDD/F emission measurements were carried out at two different diesel engines, the first one being a stationary engine for emergency power supply and the other being a modern heavy duty vehicle engine. It was shown that the emissions of dioxins and furans in both cases are nearby or lower than the overall detection limit for sampling and analysis (< 10 ng I-TEQ/m³). From these results a minor importance of PCDD/F emissions from diesel engines is indicated.

11.1.3. Background

When it became apparent that dioxins and furans could be formed during any incomplete combustion process according to the theory of „trace chemistry of fires“ [1] also motor vehicles were suspected to be dioxin emission sources [2]. Hence emissions from gasoline and diesel fuelled engines were studied several times during the last decade [3-10]. These studies being surveyed in table 1 comprise test bench experiments as well as tunnel measurements. Today it can be stated that in particular vehicles burning leaded gasoline were a considerable dioxin emission source (and they still are in those countries where this type of fuels is still used). This can be attributed to the presence of chlorinated and brominated compounds added to the fuel as so called „scavengers“ which clean the engine by conversion of lead deposits into volatile compounds.

However, only few and contradictory data were gained regarding the emissions from diesel engines. The highest emission factors for all types of vehicles were found in a study made by the California Air resources Board (CARB); however, these data were devaluated later [11] by CARB due to the small sample size and the use of low resolution mass spectroscopy. This means high detection limits and — more important — inadequate selectivity in the presence of interferences. Only one sample collected from a heavy duty diesel truck was reported because congeners from most homologue groups were detected and there were no identified interferences in this sample. No further direct emission test at heavy duty diesel engines had become known so far. Results from test bench experiments using passenger or light duty truck diesel engines respectively indicated much lower PCDD/F emissions.

Since all test bench studies failed from the possibility to make measurements at a sufficiently large number of engines, it was repeatedly tried to get indirect access to emission factors by measuring the ambient air concentration within road tunnels. While the results of the Norwegian study seem to support the CARB emission data this could not be confirmed by the Belgian tunnel experiment. From a methodological point of view, in the tunnel studies the increase of validity regarding the vehicle fleet is bought with a decrease of control of parameters which may to influence the results. In particular, re-entrainment of road dust particles into the sampling line may cause significant errors when calculating emission factors from immission concentrations.

From the data available today it can be concluded that — except for vehicles using leaded fuel — traffic is quite probably not a significant source of PCDD/F. The largest uncertainty remained regarding the emissions from heavy duty diesel engines; thus it was decided to conduct a new test bench experiment within the European Dioxin Project to evaluate whether the emission factors found by CARB more than one decade ago can be confirmed or not.

Study	Year	Country	exp. conditions	Vehicle type	number	Fuel type	emission factors			remark
							pg/m^3	pg/l fuel	pg/km	
CARB	1987	USA	bench test	light duty	1	leaded		1.794*	203*	*taken from Jones (1993); Conversion into I-TEQ with congener distribution found by Hagenmaier 1990/91 **cited in US EPA dioxin reassessment document
			steady state at 50 km/h		3	unleaded, with cat				
						diesel		4.333*	241*	
					1	diesel		3.290*	241*	
				Bus		diesel		5.904*	380*	
				truck			218**	27.440*	4.900*	
Marklund	1987	Sweden	test bench, A10 cycle	passenger car	2	unleaded			< 13	2 cycles; sampling from muffler exhaust, no scavengers
					4	leaded			20 - 220	
Bingham	1989	New Zeeland	test bench, A10 cycle	passenger car	1	unleaded			15 - 39	3 or 4 cycles; sampling from muffler exhaust
					4	leaded				

Marklund	1990	Sweden	test bench, FTP 73 test cycle	p.-car, no cat p.-car, no cat p.-car, with cat p.-car, no cat p.-car	2 2 1 2 1	unleaded leaded unleaded leaded diesel			0,36 - 0,39 2,6 - 6,3 0,36 1,1 - 2,6 not detected	FTP 73 cycle; first pair of samples and diesel sample taken before muffler, the other collected from tailpipe; leaded fuel contained with scavengers
Hagenmaier	1990/91	Germany	test bench, comparable to FTP 73 test cycle (steady state 1800 rpm, 50 Nm)	p.car, no cat p.car, with cat p.car p.car LDV	1 1 1 1 1	Unleaded unleaded leaded diesel diesel	9,8 0,93 141,5 1,20 not rep.	50,7 7,2 1.083 23,6 70	5,1 0,7 108,3 2,4 a) 35,0	fuel economy factor of 10 km/l and 2 km/l assumed for passenger cars and LDV, resp.
Bröker et al	1990	Germany	Test bench; ECE test cycle, motor oil with and without PCB	p.-car p.-car	1 1	Gasoline diesel			1.130-2.010 2.470-3.440	Sum PCDD/F (no TE values!); range reflect experiments with and without PCB enriched motor oil

Oehme et al.	1991	Norway	tunnel study	all types	>100				38 / 520 720 /9.500	cars downhill/uphill trucks downhill/uphill
Wevers et al.	1992	Belgium	tunnel study	all types P.-cars		Leaded unleaded unleaded with cat diesel	42 - 45	1.641 76,8 10,9 35,7		Emission factors derived from Hagenmaier study by comparison with tunnel study results Hagenmaiers value for passenger diesel vehicle applied.

table 1 Survey on literature data concerning dioxin emissions from gasoline and diesel fuelled vehicles

a) in the EPA document this value is erroneously reported to be 50 pg TEQ/km (obtained by multiplication with economy factor instead of division). Moreover EPA assumed that the tested diesel engine was a truck; as the second publication of Hagenmaier's group reveals the results presented in the dioxin '90 paper only refer to passenger cars.

11.1.4. Results and discussion

2 series of emission measurements were carried out at a stationary 135 kW diesel engine used for electric power generation and at a 294 kW heavy duty vehicle engine, respectively. Experimental conditions are described briefly in Annexes II and III. The intention of the measurements at the stationary engine was to test the sampling procedure and to evaluate possible difficulties with the sample clean-up. Therefore some samples were given to a private dioxin laboratory for comparison. All samples collected from the truck engine were analysed by the LUA lab solely. The measured PCDD/F concentrations in the exhaust are given in table 2. Emission concentrations are reported twice:

1. excl. DL: the reported I-TEQ value comprises only those congeners which definitely could be detected by the analytical procedure. This means, that the final mass spectrometric signal obtained for these congeners exceeded the analytical detection limit which is given by a signal to noise (S/N) ratio of 3. Concentrations of all congeners with S/N ratios below 3 were set to zero.

2. incl. DL: PCDD/F congeners with S/N ratios below 3 are included in the calculation with the concentration corresponding to their analytical detection limit (S/N=3).

The two results obtained with these different calculation procedures may be seen as best case and worst case considerations because the „real concentration“ of these congeners which could not be detected was not known exactly.

In some cases (samples EFK, D 1.0 and N 3.0) the obtained values with inclusion of the analytical detection limit are considerably higher than those only considering detected congeners. Clearly, most congeners could not be detected (see Annex II for details) and the value „incl. DL“ is mainly the result of the addition of analytical detection limits obtained for those congeners from the measured background noise.

For both engines and regardless of the specific calculation method most emission concentrations were found below 10 pg I-TEQ/m³. Unexpectedly the first control sample analysed by the external laboratory (code EDK) revealed about 10 times higher emissions. However, this difference could not be confirmed by the second control sample (code N 1.0) which was comparable to the result obtained by LUA a few days later (code N 3.0). The result of one further sample analysed by LUA (code D1.0) revealing 18 pg I-TEQ/m³ when the analytical DL is included must be considered as an artefact produced by high analytical detection limits associated with this specific analytical run (only one congener could be detected). Therefore both this sample and the first external control sample were classified as being not plausible and will not be regarded in the following considerations.

The results of the emission measurement must be evaluated in connection with the results of blank samples taken before and after each sampling. Such a comparison is presented in figure 1 and figure 2. From the blank results and their variation an „overall detection limit“ was calculated as blank mean + 3 * standard deviation of all blank results which is included in the figures as horizontal line. The high result of blank sample D 0.11 obtained with inclusion of the analytical DL was statistically proven to be an outlier compared to the other blank concentrations measured by the LUA laboratory (p=0.99, n=5). Hence this value - as well as the external blank analyses - were disregarded in the calculation of the corresponding overall detection limit (figure 1b). All emission measurement results being below the horizontal lines must be considered as not being significantly different from blank measurements. In the case of the stationary engine 3 emission results appear to exceed slightly the overall detection limit. Only 1 of 3 emission measurement results in case of the truck engine indicate a detectable emission.

.

	Sample code	date of sampling	concentration excl. DL 1) pg I-TEQ/m³	concentration incl. DL 1) pg I-TEQ/m³	sampled volume [m³] stand. cond., dry	duration of sampling [min]	Analytical laboratory
Stationary engine							
	EFK1/2	26.09.96	1,8 (0,5*/1,3**)	6,1 (1,4*/4,7**)	32,89	302	LUA
	EDK	11.03.97	58,0	61,0	10,35	246	external
	D 1.0	25.06.97	0,21	18,0	10,73	282	LUA
	N 1.0	05.08.97	6,9	6,9	10,06	255	external
	N 3.0	11.08.97	1,5	6,6	10,06	251	LUA
truck engine							
	ETE 1	09.12.97	9,7	9,7	10,03	240	LUA
	ETE 2	10.12.97	1,4	2,1	10,07	240	LUA
	ETE 2	11.12.97	1,1	2,0	9,99	240	LUA

table 2 Results of the PCDD/F emission measurements
) excl. DL: only detectable congeners (Signal/Noise ratio >3) are considered; incl. DL: congeners with Signal/Noise ratio <3 are taken into account with their analytical detection limits = Signal/Noise ratio of 3).
*** Sample compartments quartz wool cartridge and XAD 2 adsorber**
**** sample compartments condensate and rinsing solutions**

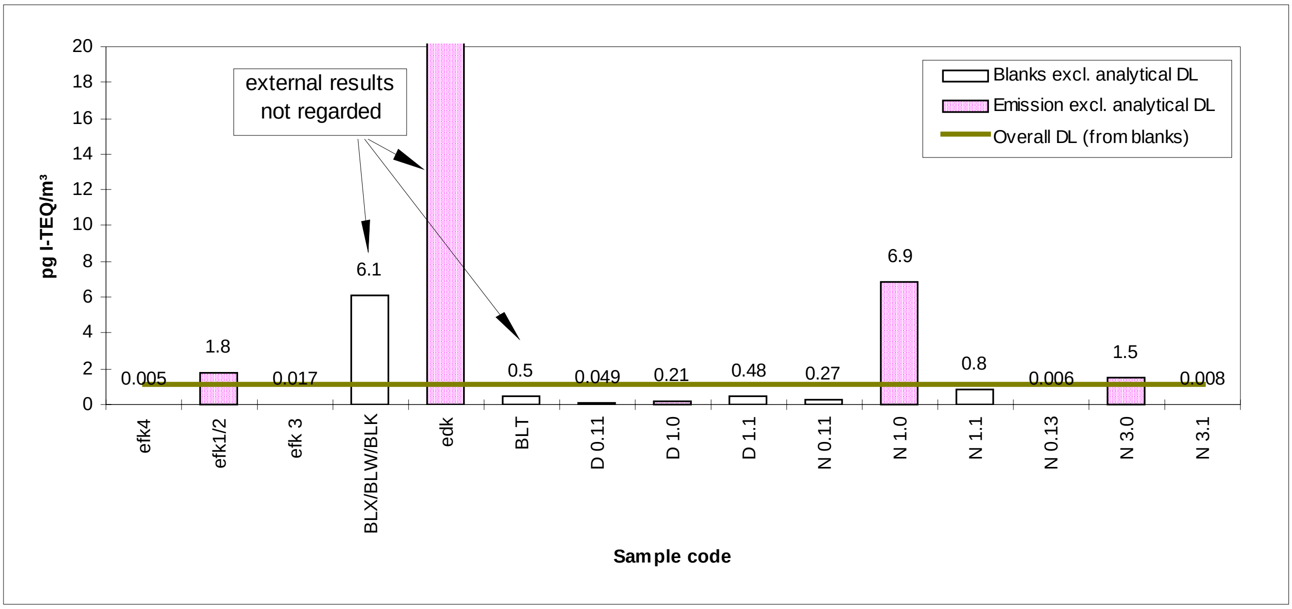

figure 1a: analytical detection limit excluded

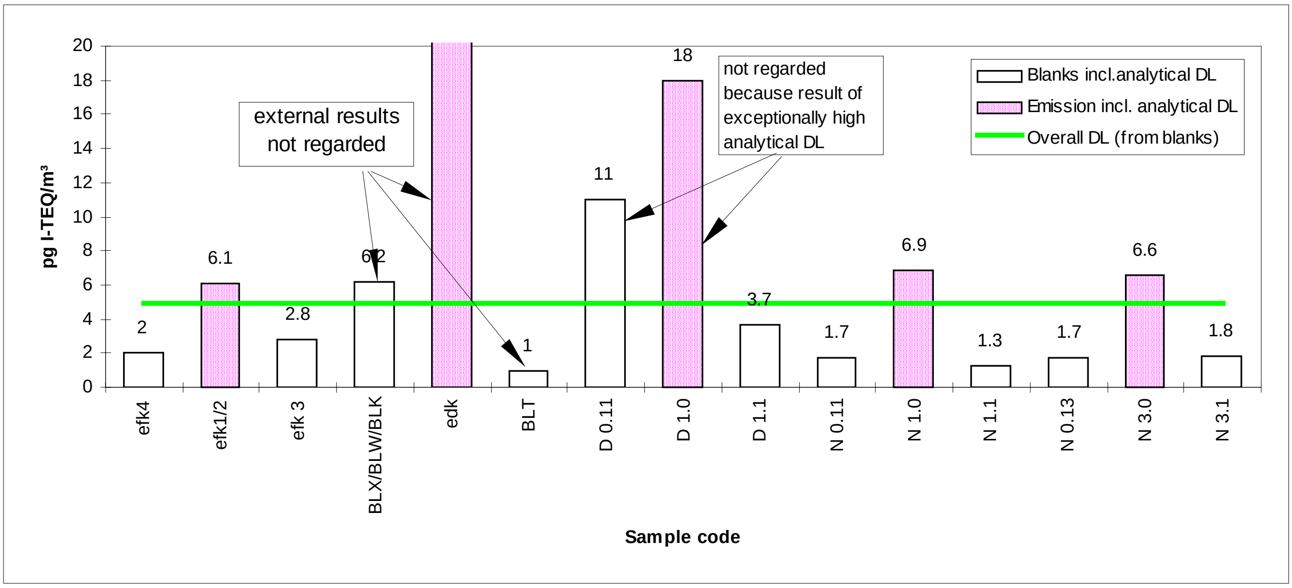

figure 1b: analytical detection limit included

figure 1: Comparison of blank values and emission measurement results of the stationary engine

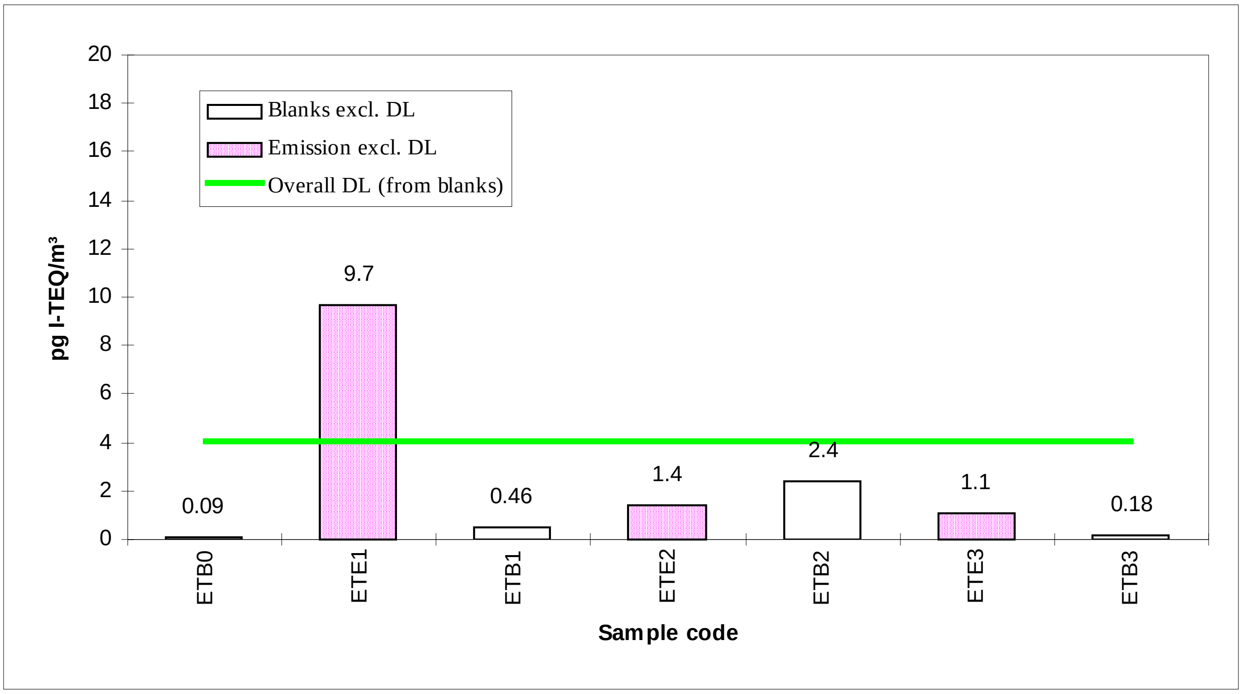

figure 2a: analytical detection limit excluded

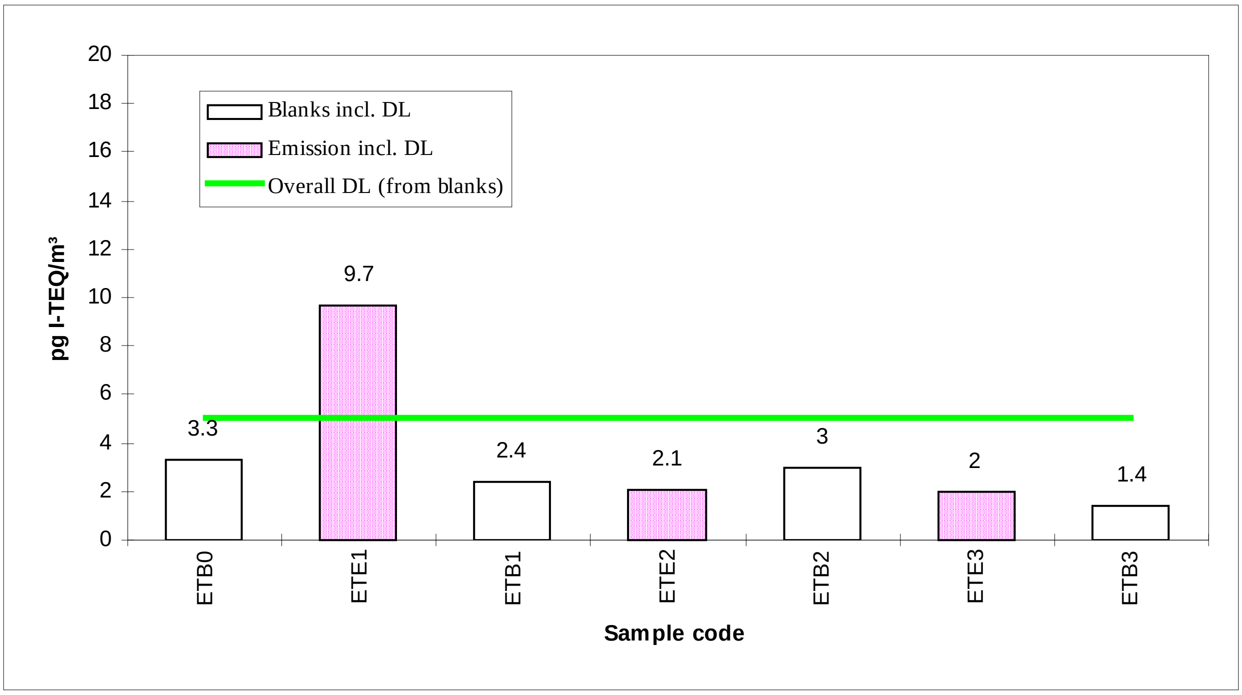

figure 2b: analytical detection limit included

figure 2: Comparison of blank values and emission measurement results of the truck engine

11.1.5. Conclusions

In view of the distribution of the measurement results around the overall detection limits and taking into account the small number of measurements it must be stated that a significant emission of PCDD/F from diesel engines is not evident. The measurements reported here, which include the first direct emission measurement at a modern heavy duty truck engine in the European region, do not support the high emissions found in the study made by the California Air Resources Board one decade ago.

Actually, the results obtained in this investigation do not allow for a calculation of reliable emission factors. However, a worst case estimate can be given in order to assess the maximum possible overall emission assigned to diesel fuel consumption. Thus from the measured emission concentrations which exceed the overall detection limit the following „effective concentrations“ may be calculated by subtraction of the mean blank values (see table 3):

	stationary engine		truck engine	
	excl. DL	incl. DL	excl. DL	incl. DL
mean blank concentration	0,2	2,1	0,8	2,5
overall detection limit	1,1	4,9	4,1	5,0
mean of results exceeding DL	3,4	6,5	9,7	9,7
effective concentration	3,2	4,4	8,9	7,2

table 3 Calculation of blank-corrected emission concentrations [pg I-TEQ/m³]

To assess an upper bound emission estimate for vehicular diesel engines the value of 8,9 pg I-TEQ/m³ was used here. With a specific exhaust volume of 30 m³/kg fuel (standard conditions, dry gas) this value is converted into an emission factor of 267 pg I-TEQ/kg fuel. The emission factor related to travel distance amounted to 107 pg I-TEQ/km with an assumed density of 0,8 kg/l for diesel fuel and an fuel economy factor of 0,5 l/km (as applied by ref. 4 for low duty vehicles). This obtained emission factor was about three times the factor reported by Hagenmaier [4] for low duty diesel vehicles. With 108.174 kt/a of consumed diesel fuel (ref. Year: 1994) in the 17 countries considered in the European Dioxin Inventory [12] a total maximum emission of about 29 g I-TEQ/a was revealed. Thus, compared to a total estimated

PCDD/F emission freight of more than 6000 g I-TEQ/a from all known sources in Europe [12] the dioxin emissions from diesel engines appeared to be irrelevant.

Note again, that this estimate did not take into account that the other results were considerably lower (below the overall detection limit of about 4 to 5 pg I-TEQ/m^3). Moreover it should be stressed, that the distribution of diesel fuel consumption to different types of vehicles (Passenger cars, LDV, HDV) was ignored for this estimation. An inclusion of this distribution is likely to lead to an even lower emission estimate due to the lower emission factors for passenger cars. Consequently, the estimate presented above may be considered as an upper bound value.

However, the calculation was based on a number of additional assumptions of which influence on the estimate could not be evaluated:

1. Assumption: the tested heavy duty vehicle engine was representative for the European diesel vehicle fleet. At the time being, this was certainly not true and in particular data for less modern truck engines would be needed for a more correct assessment; however, due to increasing efforts to reduce emissions from motor engines the modern engine tested here may be considered as representative for the near future situation in Europe.

2. Assumption: there is no influence of different diesel fuel compositions used in the various European regions. This assumption appears to be quite plausible for most of the Western European regions; but cross-contamination of diesel fuel with leaded gasoline in countries still using the latter type of fuel may be possible.

Thus there is still the possibility that the PCDD/F emissions from diesel engines were underestimated to some degree; however, even emissions higher than estimated here by a factor of 5 would not cause an alarming impact compared to a number of more important emission sources. Additional investigation would be necessary to increase the reliability of the estimate presented here; however, taking into account all measurement results on diesel engine emissions reported since 1990 it did not appear reasonable to carry out such research within the framework of the European dioxin inventory project.

References

1 Bumb, R. R.; Crummett, W. B.; Artie, S. S.; Gledhill, J. R.; Hummel, R. H. et al. Trace Chemistries of Fire: A Source of Chlorinated Dioxins. Science 1980, 210, 385-390.

2 Ballschmitter, K.; Burchert, H.; Niemczyk, R.; Munder, A.; Swerev, M. Automobile Exhausts versus Municipal Waste Incineration as Sources of the PCDD and PCDF found in the Environment. Chemosphere 1986, 15, 901-915.

3 Bröker, G.; Schilling, B.; Kirschmer, P. Chlorierte und bromierte Dioxine und Furane aus Kraftfahrzeugen; 1989, A. d. T. d. L. Ed., 1990; pp 31-34.

4 Hagenmaier, H.; Dawidowsky, N.; Weberruß, U.; Hutzinger, O.; Schwind, K. H. et al. Emission of polyhalogenated dibenzodioxins and dibenzofurans from combustion engines. Dioxin '90; Eco-Informa Press: Bayreuth, F.R.G, 1990; pp 329-334.

5 Marklund, S.; Tysklind, M.; Andersson, R.; Ljung, K.; Rappe, C. Emissions of PCDDs and PCDFs in gasoline and diesel fueled cars. Chemosphere 1990, 20, 553-561.

6 Wevers, M.; de Fré, R.; Rymen, T. Dioxins and dibenzofurans in tunnel air. Dioxin '92; VITO: Tampere, Finland, 1992; pp 321-324.

7 Anonymous Determination of PCDD and PCDF Emissions from Motor Vehicles (DRAFT); State of California Air Resources Bourd (CARB), 1987.

8 Oehme, M.; Larssen, S.; Brevik, E. M. Emission factors of PCDD and PCDF for Road vehicles obtained by a tunnel experiment. Chemosphere 1991, 23, 1699-1708.

9 Marklund, S.; Rappe, C.; Tysklind, M.; Egeback, K. E. Identification of polychlorinated dibenzofurans and dioxins in exhaust from cars run on leaded gasoline. Chemosphere 1987, 16, 29-36.

10 Bingham, A. G.; Edmunds, C. J.; Graham, B. W.; Jones, M. T. Determination of PCDDs and PCDFs in Car Exhaust. Chemosphere 1989, 19, 669-673.

11 Anonymous Estimating Exposure to Dioxin-Like Compounds-External Review Draft; Agency, U. S. E. P. Ed.; United States Environmental Protection Agency, 1994.

12 Quaß, U.; Fermann, M.; Bröker, G. Identification of Relevant Industrial Sources of Dioxins and Furans in Europe; NRW, L. Ed.; Landesumweltamt NRW, 1997.

12. Germany

12.1. Single room domestic heating stoves

12.1.1. Summary

A comprehensive investigation was made to measure the PCDD/F emissions from small single room heating stoves fuelled with different types of coal. Two stoves, typical for heating facilities of the years around 1960 and 1980 were used which operated according to the through-burning and the under-burning principle, respectively. The stoves were fed with Anthracite, hard coal briquettes, coke and brown coal from Germany, hard coal from Poland and Czech brown coal briquettes.

The PCDD/F concentrations in the flue gases ranged from around 100 up to 10.000 pg I-TEQ/m³ (at 0 % O_2). With the same fuel type, the elder through-burning oven emitted less (30 to 50%) than the more modern one. Lowest emissions were achieved with Czech brown coal, highest with Polish hard coal which previously had been shown to cause very high emissions in a test conducted by the Austrian Umweltbundesamt. However, The PCDD/F concentrations reached in our experiments never reached the Austrian results.

12.1.2. Background

Domestic combustion of fossil fuels used for room heating and/or cooking has frequently been discussed as one possible source of dioxin and furan emissions. During the last decade a number of investigations were carried out focusing on different aspects of this topic. From various studies it can be concluded that combustion of liquid or gaseous fuels in common heating appliances does not lead to significant PCDD/F formation [1, 2]. By contrast, burning of solid fuels like coal, lignite and wood may cause increased dioxin emissions [3]. Of these fuels only wood combustion, in some European countries the predominant household energy source, was suspected to be a considerable dioxin emission source [4]. This is particularly due to the high emission factors found if contaminated wood (i .e. treated with wood preservatives like PCP or wood containing other chlorinated compounds) is combusted. As the amount and composition of contaminated wood burned in households is not well known, the dioxin emission can only be estimated with high uncertainty. By contrast, whenever investigated dioxin emissions from coal combustion were revealed to be comparatively low and a default emission factor of 2 µg I-TEQ per tonne fuel was applied for the emission estimation in the report on Stage I of the DG XI European Dioxin Project [4]. Using this factor, the overall annual PCDD/F release from domestic coal combustion in 17 European countries revealed to be only around 40 g I-TEQ (less than 1 % of the total PCDD/F emission).

However, in 1998 the Austrian Umweltbundesamt presented an unexpectedly high emission factor for combustion of hard coal from Poland in a simply constructed single heating stove [5]. An application of this emission factor (range: 108 to 663 µg I-TEQ/tonne fuel at 0% O_2) would at least double the emission estimate for domestic combustion in Austria and would increase the Stage I European estimate by two orders of magnitude thus making domestic coal combustion the most relevant emission source in Europe.

LUA therefore decided to carry out a comparative measurement program in order to clarify whether the special fuel used in Austria or the stove construction or a combination of both may have caused the elevated emissions.

12.1.3. Materials and methods

The measurements were carried out at a test rig for heating facilities. The stacks used were constructed similar to those commonly found in living houses (height: ca. 20 m, bricks, rectangular shape, cross section 15*15 cm). Two stoves were tested which were taken from the collection of a Chimney Sweeper school. One of the stoves (Stove B) was a quite modern type that had been on the market about 20 years ago (produced 1983). It was a 6 kW under-burning stove with thermostat and secondary air supply. The second stove (stove A), being the elder one, operated as through-burning stove and had a power of ca. 4 kW. It was equipped with a primary air supply only and was produced between the years1955 and 1962. The ovens were connected to the stacks by stainless steel ducts about 1,5 m above ground level. The stoves were operated as commonly done by first producing a basic glowing fire through ignition of a small amount of fuel and then filling the main fuel loading onto the glowing bed. The PCDD/F samples were taken at 10 m above ground using the filter/cooler method according to VDI 3499 slightly modified by insertion of a quartz wool cartridge in front of the cooler. Sampling was not done isokinetically due to the very low flue gas velocity.

figure 1: photograph of the tested stoves

The sampling rate with a 15 mm nozzle was ca. 2 m³/h. Sampling started after the main fuel batch had reached a steady burning state. The air supply was regulated manually in order to maintain a fuel gas temperature of about 250 - 300 °C at the exit of the stove.

Six different fuels were applied. Besides the hard coal from Poland which was kindly provided by the Austrian Umweltbundesamt hard coal and lignite of German provenience (anthracite, hard coal briquettes, coke, lignite from the Rhine area) and lignite from the Czech Republic was used.

12.1.4. Results and discussion

Table 1 shows the concentrations of PCDDs and PCDFs found in the experiments. From fuel consumption determined by weighing the fuel input and the amount of residue materials after completion of the measurement fuel-related emission factors can be derived which are shown in **table** 2 .

pg I-TEQ/m^3 at 0% O_2	Stove A (operation period ~1955-65)				Stove B operation period ~ 1975-85			
Fuel type	Sample 1	Sample 2	Sample 3	**mean**	Sample 1	Sample 2	Sample 3	**mean**
Lignite Germany	197	405	396	**333**	796	493	350	**546**
Lignite Czech Rep.	292	30	20	**114**	172	199	229	**200**
Anthracite	655	352	547	**518**	1842	1178	884	**1301**
hard coal briq.Germany	778	1296	656	**910**	860	377	401	**546**
coke Germany	85	150	na	**118**	354	450	na	**402**
Hard coal Poland	2625	4494	2207	**3109**	6774	8098	15642	**10171**
na: not yet analysed; comparison with Austrian values: 13780 - 87180 pg I-TEQ/m^3								

table 1 Measured PCDD/PCDF concentrations (corrected for oxygen content)

µg I-TEQ/tonne fuel	specific flue gas volume *)	Stove A (operation period ~1955-65)				Stove B operation period ~ 1975-85			
Fuel type	Nm^3/kg fuel	Sample 1	Sample 2	Sample 3	**mean**	Sample 1	Sample 2	Sample 3	**mean**
Lignite Germany	6	1,2	2,4	2,4	**2,00**	4,8	3,0	2,1	**3,28**
Lignite Czech Rep.	5,9	1,7	0,2	0,1	**0,67**	1,0	1,2	1,4	**1,18**
Anthracite	8,4	5,5	3,0	4,6	**4,35**	15,5	9,9	7,4	**10,93**
hard coal briq Germany	8,2	6,4	10,6	5,4	**7,46**	7,1	3,1	3,3	**4,48**
coke Germany	7,2	0,6	1,1	-	**0,85**	2,5	3,2	-	**2,89**
Hard coal Poland	8,7	22,8	39,1	19,2	**27,05**	58,9	70,5	136,1	**88,49**
Comparison with Austrian values: 108,5 - 663,9 µg I-TEQ/tonne									

table 2 Emission factors derived from measured concentrations and fuel consumption.

Surprisingly, the more modern stove B generally (except for hard coal briquettes) caused higher PCDD/F concentrations in the flue gas than the more simple stove A. A possible explanation for this effect can be seen in the different condition of operation. According to the under-burning principle in Stove B the fuel was not pre-heated by the flue gases like it was the case in the through-burning stove. Hence, in Stove B cold, not yet degassed fuel entered the burning zone. This lead to a worse burn-out (indicated by higher CO concentrations) and to a higher content of volatile hydrocarbons in the flue gases which may produce higher PCDD/F concentrations. By contrast, in the more simple through-burning stove A the entire fuel batch was pre-heated and degassed during the first minutes of burning thus leading to a lower smouldering gas production at steady state conditions. However, the number of tests carried out was far too small to be shure that the difference observed between both stoves was statistically significant.

Nevertheless, compared to results obtained in previous studies all flue gas concentrations observed appear to be elevated. For instance, measurements carried out in 1992 by our own agency [3] using a 32 kW central heating unit for solid fuels did not yield concentrations above 100 pg I-TEQ/m³ (referred to 0% O_2) when any type of coal was combusted. Further, experiments made by the brown coal mining company Rheinbraun on behalf of The German Umweltbundesamt with a modern through-burning single stove (7 kW) also revealed low emissions (29 to 234 pg TEQ/m³ referred to 0 % O_2 [6]); this observation also supports the above mentioned assumption that through-burning stoves have lower emissions during steady state operation. As the stove used by Rheinbraun was a more modern one than stove B used in our experiments, a better burn-out could be achieved which coincides with lower oxygen content in the flue gas during operation (about 13% compared to ~ 18% in our experiments).

Apparently, the Polish hard coal leads to significantly elevated PCDD/F emissions compared to other fuels. Therefore, this trend is in agreement with the observation made by the Austrian UBA. In addition to the results published in 1998 further experimental investigations were reported recently by the Austrian UBA [7] which generally confirm the previous results. These observations thus can be considered as principally being plausible. However, even the highest concentration found in our tests did not reach the lowest value observed in the Austrian UBA experiments. In view of the variation of PCDD/F concentrations with stove operation conditions observed in the tests presented here it appears possible that worse combustion conditions might have caused the Austrian measurement results.

12.1.5. Conclusion

The results of the measurement program reported here reveal that PCDD/F emissions from domestic heating facilities strongly depend on the combustion conditions and the combusted fuels. While this was already known in case of different fuel types (e.g. comparing coal and wood combustion) it was generally thought that combustion of approved solid fuels like the different assortments of coal and coke would not cause any problematic emissions of dioxins and furans. However, the results presented here suggest that this view may only be true in case the fuels are combusted in larger facilities with a more sophisticated burning principle. Simple single room heating stoves and maybe open chimneys as well cause elevated dioxin emissions. The extent of these emissions is then further varying with the type of coal. Of the fuels tested the Polish hard coal purchased from the Austrian market proved to be the worst case; however, it cannot be precluded that coals imported from overseas (South Africa, Australia, USA etc.) might even be worse.

Generally, the PCDD/F emissions from domestic coal burning appear to have been underestimated during the recent years. On the other hand there is an ongoing trend in most Western European countries to substitute solid fuel heating devices by oil and gas burners. This trend most probably caused a considerable decrease of the PCDD/F emissions from domestic burning during the last 50 years.

12.1.6. Acknowledgements

LUA is greatly indebted to the North Rhine-Westphalia Chimney Sweeper Association for providing the stoves and the test stacks and for their excellent support before and during the measurement campaign. Thanks also to W. Moche of the Austrian Umweltbundesamt for his help to purchase the Polish hard coal.

References

1. G. Baumbach and H. Hagenmaier, Dioxin/Furan und BTX-Emissionen von Öl- und Gasfeuerungen kleiner Leistung, *Deutscher Flammentag 1995, VDI-Berichte* **1193**, p. 640. VDI-Verlag/Düsseldorf (1995).
2. R. Haag, N. Dawidowsky, K. H. Hermes, H. Tichaczek and G. Ludwig, Messungen der PCDD/F-Emissionen von Hausheizungen, *WLB Wasser Luft Boden*, (1992).
3. G. Bröker, K. J. Geueke, E. Hiester and H. Niesenhaus, Emissionen von PCDD/F aus Hausbrandfeuerungen, *Staub, Reinhaltung der Luft* **54**, 283-288 (6 Seiten, 8 Tabellen, 13 Quellen). (1994).
4. U. Quaß, M. Fermann and G. Bröker, Identification of Relevant Industrial Sources of Dioxins and Furans in Europe, LUA Materialien Nr. 43, 936 pp., Landesumweltamt NRW (1997).
5. W. Moche and G. Thanner, PCDD/F-Emissions from Coal Combustion in Small Residential Plants, *Dioxin '98,* Stockholm, *Organohalogen Compounds* **36**, pp. 329-332 (1998).
6. M. Erken, R. Heinen and J. Wawrzinek, N2O-, VOC- und Dioxin/Furan-Emissionen aus festbrennstoffgefeuerten Kleinfeuerungsanlagen, UBA-FB 96-082, p. 463. Umweltbundesamt Berlin, Rheinbraun AG, Köln (1996).
7. W. Moche and G. Thanner, PCDD/F Emissions from Domestic Heating with Wood, Coal and Coke, *Dioxin 2000,* Monterey, California, 13.-17.08. *Organohalogen Compounds* **46**, pp. 295-297 (2000).

13. Greece

13.1. Measurements at 3 plants

13.1.1. Summary

The very first PCDD/F emission measurements at industrial installations in Greece are reported. Sampling and analysis was done by an experienced German institute. Of the facilities investigated, an electric steel plant proved to have the highest annual emission of about 1 g I-TEQ/year. Relating the production rate of this plant to the statistically reported entire Greek production it is assumed that 4-5 g I-TEQ will be released to air. from this process annually. A lower annual emission, but much higher flue gas concentrations exceeding the scheduled European emission limit of 0,1 ng I-TEQ/m³ by more than a factor 3000 were found at a hospital waste incinerator. This finding is a confirmation of the Stage I assessment regarding this process. Annual emissions of about 35 g I-TEQ/year can be estimated from statistical data. Finally, a rotary kiln process for drying residual materials from olive oil production was found to be negligible with regard to emissions of dioxins and furans.

13.1.2. Background

Greece was one of the Western European countries of which no information on dioxin and furan emission could be obtained for during Stage I. Therefore, it was one of the Stage II aims to initiate first emission measurements at possibly relevant facilities in this country.

Fortunately, a German research institute which is known to be an experienced and reliable partner could be found for this sub-project. The institute previously had published their measurement results obtained at a Greek waste dump and through this work had some contacts to a Greek environmental institute that could assist in selecting the facilities to be measured.

As no support by governmental institutions could be achieved for this project it was a matter of agreements between plant operators and the involved institutes whether measurements could be done or not. Hence, some facilities that originally were on the list of probably relevant plants (e.g. secondary aluminium smelters, and other non-ferrous metal processing installations) could not be included.

13.1.3. Results and discussion

Finally, 3 plants could be investigated:

- A **small hospital waste incinerator** which is said to typically represent similar facilities operated in every middle-size town in Greece. The incinerator is operated for ca. 3 hours per day, sometimes even on Saturdays but never on Sundays. Thus the annual operation time is estimated to about 900 hours. Input of clinical waste (e.g. syringe residues, plastic bags, human organic materials, etc.) is about 20 to 30 bags per hour; the weight or volume of these bags was not reported. Flue gas cleaning is achieved by a post-combustion chamber only. Flue gas volume (dry, standard conditions) amounted to about 1200 m³/hour. Sampling for PCDD/F was done at the end of the stack which is only 15 m high with a diameter of 0,32 m.
- An **electric arc steel plant** where steel scrap from Greece and from eastern Europe is processed. It is a batchwise operated facility; each smelting cycle takes between 45 and 70 minutes with interrupts of 15-25 minutes. Per operation cycle about 75 tons of iron scrap is smelted applying 35 MW of electric power. Flue gases from this installation are collected by two separate means: — first, from the inner part of the smelting reactor by suction through the hood of the reactor (“primary flue gas”, ~ 450.000 m³/h standard dry); — secondly, the air of the hall built around the smelter is actively drawn out by means of several suction points (“secondary flue gas”, ~ 170.000 m³/h standard dry). Both gas streams are dedusted by fabric filters and enter the ambient atmosphere through separate stacks (45 m height / 4,3 m diameter and 40 m height / 3,2 m diameter, respectively). Sampling of PCDD/F took place in both flue gas ducts downstream of the fabric filters.
- An installation for **pyrolytic drying of residuals from olive oil production**. This facility is part of an installation which makes use of the solid residues of an olive oil production plant. In this process the oil is first extracted from the fruits by mechanical pressing without heating. The solid residues of this process are then dried by means of a rotary kiln heated to ca. 350 °C. The drying step is followed by a chemical extraction process using n-hexane as solvent for the recovery of olive oil and fats still contained in the residues. The residues, now being almost dry and free of fatty substances are transferred into a combustion furnace generating the heat needed for the drying rotary

kiln. Olive oil dissolved in n-hexane is separated by a fractionating freeze process. The flue gases from the drying kiln (~ 13.000 m³/hour) are dedusted by a two stage cyclone before entering ambient air through a 20 m stack (cross section about 1 m²). The entire drying/combustion plant consist of two identical lines which process together ca. 20.000 tons per year. The facility is operated discontinuously only at daytime and only during the harvest season. PCDD/F sampling was carried out at one line downstream of the first cyclone stage.

Sampling was carried out using a filter/cooler apparatus according to VDI 3499/EN 1948. which consisted of a condensate flask, a quartz glass wool filter and XAD-2 adsorbent resin. The samples were transported to Germany and analysed at the GSF institute; per each campaign a 50% aliquot of one sample extract was cross-check analysed at the LUA laboratory. All cross-check results proved to be in acceptable agreement as shown in table 1.

Sample	GSF ng I-TEQ/m³	LUA	Deviation %
OLIVE02	0,057	0,079	38,6
Hosp3	291	270	7,2
IronB01	0,53	0,62	17,0
IronA02	0,034	0,012	64,7

table 1 Comparison of analytical results obtained from the cross-check samples

The results of the 4 measurement campaigns are summarised in table 2.

Facility	Mean PCDD/F concentration	Flue gas volume	PCDD/F Mass flow	Annual operation time	Annual emission
	ng I-TEQ/m³	m³/h	µg I-TEQ/h	hours	g I-TEQ/a
Hospital waste incinerator	324,8	1108	360	900	0,3
Steel plant primary dedusting	2,1	171565	123	3.000	0,4
Steel plant secondary dedusting	0,3	449019	361	3.000	1,1
Olive oil plant pyrolytic drying	0,3	13237	4	1.000	0,004

table 2 Results of PCDD/F emission measurements at Greek installations

The PCDD/F concentration found in the flue gas of **the hospital waste incinerator** is very high and reaches values that have been observed before at similar facilities only a few times. However, due to its limited operation time the annual emission from this facility is less significant. Nevertheless, the emission must be regarded as relevant because a local impact of this installation is likely due to the low stack height of only 15 m.

According to statements of the operator there are plenty of similar installations operated in Greece. All together these installations, if showing similar emissions too, would have a significant environmental impact. From the measured data and using a specific flue gas generation rate of 7.000 m³/ton waste the emission factor of the investigated plant is calculated to be approximately 2.000 µg I-TEQ/ton. This is only 20% less than the default emission factor of 2.500 µg I-TEQ/ton chosen for Greek hospital waste incinerators in the Stage I report. Hence the annual emission of 37 g I-TEQ/year for this sector was not much overestimated.

Despite much lower flue gas concentrations the annual emissions from the **electric arc steel** plant are higher. Considering the operation data mentioned above it is assumed that on 300 days per year 10 smelting cycles are carried out. Thus the annual operation time is about 3.000 hours yielding ca. 1 g I-TEQ/year of annual emission. With 75 tons per each cycle (or 225 kt per year) the emission factor of the measured steel plant can be calculated to be 4,4 µg I-TEQ/ton. This factor compares well to values reported from other countries which range from < 1 to ca. 10 µg I-TEQ/ton (c. f. Stage I report, p. 140). In the stage I report the 1995 production rate for electric arc furnaces in Greece was reported to be ca. 900 kt. Thus the emission from this industrial process could have been ca. 4 g I-TEQ in 1995. This is nearly the maximum estimate and about 4 times the typical value used for the European inventory in Stage I.

The olive residue drying facility, finally, did not emit PCDD/F in considerable amounts. This is somehow unexpected since the drying process is carried out at temperatures which are favourable for a de-novo-formation of dioxins and furans. A possible explanation could be the lack of enough chlorine; this, however, can be clarified only by additional analysis of the residues.

13.1.4. Conclusion

The results of the Greek measurement program again highlight the importance that hospital waste incineration still may have with respect to the releases of dioxins and furans in some European countries. Due to the mostly small installations with low-height stacks most of the emissions is likely to be deposited in the vicinity of the plants which often are located at or nearby hospitals. A waste management system to collect the wastes from hospitals and other institutions of the health care sector in connection with a state of the art waste treatment is therefore highly recommendable.

The emission found at the electric arc steel plant confirms the emission factors found in other countries and therefore leads to an increased certainty of emission estimates for this industrial sector.

Greece has a number of further industrial, potentially dioxin relevant activities (like metal scrap incineration, cement production, secondary non-ferrous metal smelters [1]). Thus further investigation is recommended if a decrease of dioxin emissions from industrial sources shall be achieved.

Besides, substantial emissions have been suspected by the Greek Greenpeace office [2] to be caused by accidentally or intentionally induced landfill fires. Due to uncertainties regarding the emission factors of these sources possible emissions were assessed to range from 50 to 920 g I-TEQ/year. Elevated soil contamination with PCDD/Fs found in the vicinity of a dump site on Crete [3] appear to support the possible importance of this emission source. Due to the near-ground emission it cannot be expected that a large fraction of emitted dioxins and furans are subjected to long-range transport.

References

1. Kouimtzis, T., et al. PCDD/Fs and PCBs Concentrations in the Ambient Air of the Greater Thessaloniki Area/Greece. in Dioxin 2000. 2000. Monterey, California.
2. Psomas, S., Personal Communication. 2000.
3. Marten, D., et al., Chemical Impact of uncontrolled solid waste combustion to the vicinity of the Kouroupitos Ravine, Crete, Greece. Chemosphere, 1998. **36**(14): p. 2855-2866.

14. Portugal

14.1. Emission measurements at various industrial facilities

14.1.1. Summary

Within a co-operative subproject being equally funded by the Stage II project and the Portuguese government and involving a German and a Portuguese laboratory a number of potential PCDD/F sources in Portugal were investigated. As far as is known, the emission measurements reported here are the very first PCDD/F emission tests carried out in Portugal. These included 3 hospital waste incinerators (two old ones and one new state-of-the-art installation) , an electric arc furnace steel plant, a secondary aluminium smelter and a secondary copper smelting facility. Very high PCDD/F concentrations in the flue gas of about 100 ng I-TEQ/m³ were found at one of the old hospital waste incinerators, while the second old facility had surprisingly low emissions (~ 2 ng I-TEQ/m³). As expected, the new facility emitted far less than 0,1 ng I-TEQ/m³. With respect to the PCDD/F mass flow rate the steel plant proved to be the worst installation accounting for annual emissions of nearly 1 g I-TEQ. All together the 6 plant’s contribution to the annual dioxin emission is about 1,7 g I-TEQ which may account for 3-10% of the estimated industrial emissions for 1995 in Portugal.

14.1.2. Background

Quite in an early stage of the project the Portuguese ministry of Environment sent a letter of interest and indicated its will to take part in an investigation on dioxin sources in its country. However, as no laboratory was known in Portugal being capable to carry out dioxin emission measurements a measurement program appeared difficult to realise. Fortunately, a well-known German laboratory having good business contacts to a Portuguese engineering company offered to participate and to take over the duties of supervising the dioxin sampling campaigns and the analysis. The costs for this project were financed from funds of the Stage II project and by the Portuguese ministry at equal parts.

From the Stage I inventory hospital waste incineration revealed to be the main industrial emission source. Further sources, including an iron ore sintering plant, were likely to exist in the metallurgical industries. LUA emphasised the importance of testing the sinter plant; however, to get the measurement permission soon appeared difficult and it was decided not to insist in that measurement in order to guarantee the realisation of the program.

14.1.3. Results and discussion

Emission measurements were carried out at:

- three hospital waste incinerators,

  I: Hospital SJ: Two controlled-air incinerators. Emission samplings were performed in just one of them, but they work at the same time. There is no gas treatment, just a heat recovery system has been installed. The stack height is 12 m above ground level.

  The incinerators work 300 days per year yielding about 2.700 hours of operation. The capacity of both incinerators is 12 tons/day but they are just working with 8 tons/day. The amount of waste incinerated in the line measured was 2.634 kg in the first sampling, and 2.796 kg in the second one

  II. Hospital SA: two controlled-air incinerators, but just one is working, line 2. There is no gas treatment, just a heat recovery system has been installed but it is out of operation too. There is a ventilator that introduces air into the duct before the stack to cool the temperature of the gas. The stack height is 30 m above ground.

  The incinerators work 2 days per week and have a capacity to incinerate 350 kg/h however they are working with less waste, 250 kg/day. The annual operation time is ca. 312 hours only. The amount of waste incinerated was 485 kg in the first sampling and 700 kg in the second one.

  III. Hospital JdM.: One controlled-air incinerator, with a capacity to burn 550 kg/h. The gases produced in the incineration process go through a heat recovery system and a gas treatment system. There are sodium bicarbonate and dry activated carbon injection into the flue gas for treatment. The system has also a battery of ceramic filters. Stack gases are emitted 11 m above ground; the annual operation time is 2496 hours. During sampling the amount of waste incinerated was 4281kg

- two different stacks of an electric arc steel plant where steel scrap is recycled into liquid steel with an electric arc furnace having a capacity of 80 ton/batch. Gaseous emissions of the furnace are split into 2 ducts (old system and new system) leading to a cooling system and to a fabric filter prior to release into the atmosphere. The plant operates continuously with 2 yearly maintenance stops of 2 weeks each.

and two processes of the non-ferrous metal industry:

- secondary aluminium production

  This plant uses aluminium scrap as raw material, it has a capacity to produce 550 tons per month but at the time of measurement it was only producing 200 tons/month. The metal smelting is done 5days/week between 8 am and 16 pm and the plant stops in August. This makes up 1920 hours of operation per year.

  In the smelting section there are four groups of furnaces that can work individually or simultaneously. In each group there are two furnaces, one for the smelting and the second one for the toning of alloys. During the smelting process, salts like sodium chloride, potassium chloride and a fluoride are added to avoid the contact between alloys and the air. It is used tick fuel containing 3,5% sulphur for the heating of the furnaces. There is just one exhaustion system for all furnaces. There is no system for gas purification. The stack gases are released at 21 m above ground.

  During the first sampling furnaces nº 1, 2 and 3 were working, the total amount of smelting scrap was 11.174,5 kg and 9.998 kg of aluminium ingots were produced. In the second sampling the scrap used was 7.554 kg and there was an aluminium ingots production of 7.554 kg.

- secondary copper smelter

  This plant uses brass scrap as raw material to produce brass ingots. In the smelting section there are three smelting furnaces and two others for liquid metal maintenance. All furnaces have electric heating and they are equipped with exhaustion system connected with two gas treatment lines that include refrigerators, cyclones and fabric filters. Stack gases leave at 20 m above ground; the annual operation time is about 8.064 hours. During the sampling, only one smelting furnace and one maintenance furnace were operating. During both samplings the total amount of smelting scrap was 28 tons and 26 tons of brass ingots were produced

Sampling and analyses were done according to EN 1948 except for some restrictions with respect to sampling which were posed by plant peculiarities. The results are briefly shown in table 1.

Portugal *Emission measurements at various industrial facilities*

Plant	sample code	date	PCDD/F concentration		Flue gas flow rate	PCDD/F mass flow
			ng I-TEQ/m³		m³/h	µg I-TEQ/h
			extern. lab.	LUA		
Steelplant, old system	132	09.12.99	0,175	0,46	99638	17,4
	134	10.12.99	0,246	-	89347	22,0
Steel plant, new system	136	11.12.99	0,473	0,66	242583	114,7
	138	12.12.99	0,319	-	237385	75,7
Hospital waste incinerator SJ	140	14.12.99	94,48	126	1029	97,2
(one line of two)	142	15.12.99	66,85	-	961	64,2
Hospital waste incinerator SA	144	07.12.99	0,45	0,56	7322	0,9
	146	17.12.99	2,74	-	8122	22,3
Sec. Aluminium smelter	336	04.04.00	12,5	-	26557	332,0
	337	05.04.00	1,99	3,4	29444	58,6
Hospital waste incinerator JdM	338	07.04.00	0,02	-	3721	0,1
Recycling copper smelter	339	11.04.00	0,02	-	71213	1,4
	340	12.04.00	0,004	0,0053	70299	0,3

table 1 Results of PCDD/F emission measurements at various facilities in Portugal

The measured concentrations of dioxins and furans covered more than 4 orders of magnitude from far below up to a hundred-fold of the incinerator limit value of 0,1 ng I-TEQ/m³. Cross check analysis results generally agree with the results obtained by the external laboratory.

The most remarkable stack gas contamination was — not unexpectedly — found at a hospital waste incinerator. The cross check result was less satisfying in this case; from data provided from the external laboratory it revealed that this might be due to a dilution of the extract — which has not been done at LUA’s dioxin lab — prior to analysis. Thus the analyses were carried out at very different effective concentrations injected into the GC/MS.

Nevertheless, a very high emission level is indicated for this hospital waste incinerator. This result on one hand justifies the Stage I approach for the estimation of PCDD/F emissions from hospital waste incineration in Portugal; on the other hand, the emission factor of 2.500 µg I-TEQ /ton assumed in the stage I report was not reached (c.f. Taking into account that other hospital waste incinerators showed considerably less emissions it must be concluded that the previous emission value for this sector presented in the Stage I report was an overestimation. Nevertheless, this particular facility should be shut-down or at least upgraded since — due to the low stack height of 12 meters — it is likely to pollute the nearby area considerably.

Plant	Duration of sampling hours	Production kg	Activity rate tonnes/h	emission factor per measurement µg I-TEQ/tonne	mean µg I-TEQ/tonne
Steelplant, old system	5,57	462,000	82,9	0,21	**0,24**
0	5,6	460,000	82,1	0,27	
Steel plant, new system	5,72	481,000	84,1	1,36	**1,17**
0	5,8	447,000	77,1	0,98	
Hospital waste incinerator SJ	5,83	2,634	0,5	215,2	**174,57**
(one line of two)	5,83	2,796	0,5	134,0	
Hospital waste incinerator SA	3,73		0,121	7,3	**67,24**
0	3,63		0,175	127,2	
Sec. Aluminium smelter	5,67	10	1,8	188,2	**115,28**
0	5,42	7,5	1,4	42,3	
Hospital waste incinerator JdM	6	4,281	0,7	0,1	**0,1**
Recycling copper smelter	6	26	4,3	0,3	**0,20**
0	6	26	4,3	0,1	

table 2 Calculation of emission factors for sampling periods from production/consumption data of the tested plants and the mass flow rates shown in table 1

A ranking list according to PCDD/F annual releases (table 3) clearly shows, that with respect to the overall release of PCDD/Fs to the atmosphere the steel plant is more important than the incinerators, whereas the emissions from aluminium production equal those of the SJ hospital incinerator. The aluminium plant may account for nearly 0,4 g I-TEQ/ year; in view of a stack height of only 21 meters it is very likely that a large part of the emitted pollutants will be disposed off in the vicinity of the plant. The enormous dust concentration of nearly 2 g/m³ in the stack gases indicates that this plant is equipped with an absolutely inadequate de-dusting systems. However, this also means that abatement of PCDD/F emissions might be achievable in this case at moderate costs by upgrading just the dust filters to modern up-to-date technology. Assuming that a reduction of dust concentrations to at least 50 mg/m³ is achievable and that dioxin concentrations will decrease correspondingly the future PCDD/F emissions from that plant may be only around 20 mg I-TEQ/year or even less.

In case of the steel plant the PCDD/F concentration as well as dust content are at a “normal” level and therefore any further abatement presumably would need considerable effort. Hence this plant most probably will remain one of the most important PCDD/F emission sources in Portugal.

Plant	mean PCDD/F concenration *)	Flue gas flow rate	PCDD/F mass flow rate	Annual operation time	Annual emission	dust conc.
	ng I-TEQ/m³	m³/h	µg I-TEQ/h	h	g I-TEQ/a	mg/m³
Steel plant, new system	0,4	239984	95,2	7680,0	0,73	20
Hospital waste incinerator SJ *)	80,7	995	161,5	2700,0	0,44	150
Sec. Aluminium smelter	7,2	28001	195,3	1920,0	0,37	1800
Steelplant, old system	0,2	94493	19,7	7680,0	0,15	20
Recycling copper smelter	0,01	70756	0,9	8064,0	0,0069	5
Hospital waste incinerator SA	1,6	7722	11,6	312,0	0,0036	nd
Hospital waste incinerator JdM	0,02	3721	0,1	2496,0	0,0002	10
Total			**484,2**		**1,7**	

(at operative oxygen); *) calculated for both lines assumin similar concentrations and flow rates

table 3 Ranking list of investigated emission sources with respect to their annual PCDD/F emissions

14.1.4. Conclusion

The emission measurement program carried out in co-operation of a Portuguese and a German private institute with co-funding by the Portuguese ministry of environment and - through LUA – by DG Environment has successfully identified relevant sources of emissions in this particular country. Since all information available before was entirely based on estimation [1], the state of knowledge has been considerably improved. With regard to the relevance ranking list developed in Stage I of the European Dioxin Inventory Project further emission testing is urgently recommended to be done at the iron ore sintering plant. As the results obtained at the aluminium smelter indicate immediate attention should be paid to all thermal sources with apparently high dust emissions (dust emissions of above 100 mg/m³ may easily be discovered due to their visibility at the stack exit).

Comparing the annual emission of the 6 plants investigated to the overall emission estimate for industrial sources in Portugal of 15-50 g I-TEQ/a (c.f. Vol. 3) they may account for about 3 to 10 per cent. Further activity to identify and characterise industrial emission sources appears therefore necessary [2]. The first step on this way has been made by the Portuguese government through supporting the measurements reported here. From European environment’s point of view this must be greatly appreciated.

References

1. M. Coutinho, C. Borrego and C. Ferreira, Atmospheric Emissions of PCDD/PCDF and Heavy Metals in the Oporto Urban Area, *Dioxin '98*, Stockholm, *Organohalogen Compounds* **36**, pp. 153-156 (1998).
2. M. Coutinho, R. Rodrigues, U. Düwel, O. Päpke, C. Borrego and Schrö, The DG ENV EUROPEAN DIOXIN EMISSION INVENTORY- STAGE II: Charactarization of the emissions of 2 hospital waste incinerators and a steel mill in Portugal, *Dioxin 2000,* Monterey, CA, 13.-17.08.2000. *Organohalogen Compounds* **46**, pp. 287-290 (2000).

Glossary and list of abbreviations for Volumes 1-3

µg	**m**icro**g**ram (10^{-6} g)
2,3,7,8-TCDD	2,3,7,8-**T**etra**c**hlorodibenzo-**p**ara-**d**ioxin (“Seveso dioxin”)
a	Annum
Ahh	**A**ryl **h**ydrocarbon **h**yroxylase, enzyme used in bioassays as an indicator for Ah-receptor activity
Airfine	Emission abatement system for iron ore sintering plants sold by the company Voest-Alpine, Austria
Alicyclic compounds	Chemical compounds with a cyclic structure build only from carbon atoms
Aroclor®	Trade name of technical mixtures of polychlorinated biphenyls
CO	Carbon monoxide
CO_2	Carbon dioxide
CYP1A1	Specific cytochrome P 450 enzyme, induced by dioxin-like compounds through affection of the Ah receptor
CYP1A2	Specific cytochrome P 450 enzyme, induced by dioxin-like compounds through affection of the Ah receptor
d	**D**ay
d.s.	**d**ry **s**ubstance
DNA	**D**esoxyribo**n**ucleic **a**cid
Dibenzofurans	Class of chemical compounds; often used as a short form for polychlorinated dibenzofurans
Dibenzo-p-dioxins	Class of chemical compounds; often used as a short form for polychlorinated dibenzo-p-dioxins
EC	**E**uropean **C**ommunity
EDC	**E**thylene**dic**hloride (1,2-Dichloroethane)
EPA	**E**nvironmental **P**rotection **A**gency
EROD	7-**e**thoxy**r**esorufin-**O**-**d**iethylase, enzyme used in bioassays as an indicator for Ah-receptor activity
ESP	**E**lectro**s**tatic **P**recipitator
Eurostat	Statistical office of the European Community
fg	**f**emto**g**ram (10^{-15} g)
HCW	**H**ealth **Care** **W**aste
Heterocyclic compounds	Chemical compounds with a cyclic structure build from carbon atoms and at least one other element
HWI	**H**azardous **w**aste **i**ncineration
I-TEF	**I**nternational **T**oxic **E**quivalence **F**actor according to the NATO/CCMS list
I-TEQ	**I**nternational **T**oxic **E**quivalent; unit based on the I-TEFs and used to express the toxicity of a mixture of PCDDs and PCDFs compared to the so-called Seveso dioxin
Keramsit	Product from natural zeolithes; used e.g. for water filtration
kg	**K**ilo**g**ram
L.D.	**L**ethal **d**ose
mg	**M**illi**g**ram (10^{-3} g)
Mpa	**M**ega **Pa**scal, pressure unit, (10^{6} Pascal)
MSW or msw	**M**unicipal **S**olid **W**aste
n. d.	“not detectable”; “no data”, “not determined”

NATO/CCMS	**N**orth **A**tlantic **T**reaty **O**rganisation/**C**ommission for **C**hallenges of **M**odern **S**ociety
Ng	**n**ano**g**ram (10^{-9} g)
Nm^3	Normalised cubic meter, volume of a gas at 1013 hPa and 0° Celsius
NOAEL	**N**on **o**bservable **a**dverse **e**ffect **l**evel
N-TEQ	**N**ordic **T**oxic **Eq**uivalent, commonly used in Scandinavian countries to express the toxicity of a mixture of PCDDs and PCDFs compared to the so-called Seveso dioxin
PCDD	**P**oly**c**hlorinated **d**ibenzo-para-**d**ioxins
PCDD/F	PCDD and PCDF
PCDF	**P**oly**c**hlorinated **d**ibenzo**f**urans
PCDT	**P**oly**c**hlorinated **d**ibenzothiophene (sulphur analogue compound of PCDF)
PCP	**P**enta**c**hloro**p**henol
PCTA	**P**oly**c**hlorinated thianthrene (sulphur analogue compound of PCDD)
pg	**P**ico**g**ram (10^{-12} g)
POPs	**P**ersistant **o**rganic **p**ollutant**s**, group of different chemicals known to accumulate in the environment; include PCDDs and PCDFs
PVC	**P**oly**v**inyl**c**hloride
Seveso dioxin	2,3,7,8 – tetrachlorodibenzo-p-dioxin
SNAP	**S**elected **N**omenclature for **A**ir **P**ollution
SO_2	Sulfur dioxide
Sorbalit®	class of adsorbents based on lime and activated coal components
TEF	**T**oxic **E**quivalence **F**actor, in general
TEQ	**T**oxic **Eq**uivalent, in general
Thianthrene	Heterocyclic compound with structure similar to the alicyclic anthracene but with 2 sulphur atoms bridging the outer carbon rings
Thiophene	Sulphur analogue compound of furan
throughburner	Operation principle of solid fuel heating stoves; flue gases generated from the burning layer at the bottom of the fuel load flow through the fuel load before entering the chimney
Underburner	Operation principle of solid fuel heating stoves; flue gases generated from the burning layer at the bottom of the fuel load are drawn away and do not flow through the fuel load before entering the chimney
Vol.	Volume
WHO	**W**orld **H**ealth **O**rganisation

ANNEX 1

Spreadsheet report forms

Plant operation conditions during measurement

General operation conditions

Plant was operated continuously (yes/no)		
Plant was operated intermittently (yes/no)		

In case of intermittent operation:

duration of operation cycles ranged between		hours:min and		hours:min
duration of plant operation interrupts ranged between		hours:min and		hours:min

In case these conditions are untypical for the plant, please explain:

Input materials (during measurement!)

Number	name	Input [tons/hour]	composition	remark

Flue gas components and density

Measurement of flue gas components			Remarks
N_2 (dry gas)		% (v/v)	
O_2 (dry gas)		% (v/v)	
CO_2 (dry gas)		% (v/v)	
Ar		% (v/v)	
CO (dry gas, optional))		% (v/v)	
SO_2 (dry gas, optional)		% (v/v)	
other compounds (please fill in)		% (v/v)	*insert standard density in table below!*
other compounds (please fill in)		% (v/v)	*insert standard density in table below!*
dust (if known)		mg/m³	*please specify measurement conditions!*
Moisture (absolute water content)		kg/m³	
static pressure in stack		**k**Pa	*insert differential pressure; = p(stack)-p(atmos); e.g. -0.3*
atmospheric pressure		**k**Pa	
mean gas temperature		°C	*insert here in case no temperature profile is measured*
...used for t-correction:		°C	*value is selected automatically (either mean of profile measurement or mean gas temperature given above)*

Calculation of gas density

T,p- correction term
Humidity correction term

compound	**standard density kg/m³**	**volume fraction Total = 000**	**partial density kg/m³**
N_2	**1,251**		
O_2	**1,429**		
CO_2	**1,977**		

Circular stack profile (acc. to ISO 9096:1992)

Note: Number and location of sampling points should be determined according to ISO 9096:1992, Annex B;

Location of sampling points is calculated with tangential rule (annex B.2)

Stack height		m	
Stack diameter		m	
Stack cross section		m²	
number of sampling lines	4		
number of sampling points per line			
recommended:			
actual:			
Pitot correction factor			*(=1 for standard Pitot tube = Prandtl tube)*

Sampling point No.	distance from port mm	weight factor -	dyn. pressure kPa	gas velocity [m/s]		temperatur
				calculated from p	directly measured	measured
	First sampling line					
	replace by actual values!					
1		1				
2		1				
3		1				
4		1				
5		1				
6		1				
7		1				
8		1				
9		1				
10		1				
	Second sampling line					
11		1				
12		1				
13		1				
14		1				
15		1				
16		1				
17		1				
18		1				
19		1				
20		1				
mean (operation conditions)						
maximum (operation conditions)						
mean (standard conditions, dry)						
maximum (standard conditions, dry)						
CIRCMAX value used for nozzle selection:				0,00		

Specify method in case of direct velocity measurement:

Rectangular stack profile (acc. to ISO 9096:1992)

Note: Number and location of sampling points should be determined according to ISO 9096:1992, Annex B;
Use the values for Ki tabled therin

Stack height		m	
Long side of stack L_1		m	
Short side of stack L_2		m	
Stack cross section		m^2	
number of sampling points *recommended:* actual:			
Pitot correction factor			*(=1 for standard Pitot tube = Prandtl tube)*
static pressure in stack		kPa	*differential pressure; = p(stack)-p(atmos)*
atmospheric pressure		kPa	

Sampling point No.	distance from...[mm] ...L_1	...L_2	weight factor -	dyn. pressure kPa	gas velocity [m/s] calculated from p	directly measured	temperatu measured
overwrite with actual values!							
1			1				
2			1				
3			1				
4			1				
5			1				
6			1				
7			1				
8			1				
9			1				
10			1				
11			1				
12			1				
13			1				
14			1				
15			1				
16			1				
17			1				
18			1				
19			1				
20			1				
mean (operation conditions)							
maximum (operation conditions)							
mean (standard conditions, dry)							
maximum (standard conditions, dry)							
RECTMAX value used for nozzle selection:					0,00		

Specify method used for direct velocity measurement:

Nozzle&Sampling Rate

Nozzle selection for...

...maximum flue gas velocity		**m/s**	standard conditions, derived from measured maximum flow rate
...maximum sampling flow rate:	**2**	**m^3/h**	standard conditions, as given by the equipment used

maximum nozzle diameter [mm]	chosen nozzle [mm]	nozzle cross section [m^2]

Conversion factor		factor used to determine sampling flow rate at standard conditions from measured flue gas velocity at the sampling points in stack

Chosen sampling flow rate (at standard conditions!):	

First sampling line

sampling point No	flow rate [m^3/h]			remarks
	recommended	actually chosen *)	isokinetic?	
1				
2				
3				
4				
5				
6				

Sampling Protocol

Sampling location at duct:			
Sampling Train			
Name of method			
Scheme			
Sampling flow rate measurement with	*specify instrument, e.g. orifice/pressure or rotameter*		
	value	dimension	Remarks
Probe diameter		mm	
Filter diameter		mm	
Filter efficiency (%, manufacturer's data)		%	
Ab/adsorbent (type)			
Ab/adsorbent, amount		g	
In case of flow division:			
Mean flow rate through filter		m³/h	
Mean flow rate through Ab/adsorbent		m³/h	
Sampling data	value	dimension	Remarks
Leak check by plugged nozzle:			
Lowest pressure when pump on:		kPa	
Rate of pressure change when pump off		kPa/min	

Extraction/Clean-up

Sample treatment after the measurement campaign

sample storage location			
temperature at storage		°c	
	dd:mm:yy	hh:mm	
start of storage (date, time)			
end of storage (date, time)			
addition of extraction standard			short description of extraction/clean-up procedure:
start of extraction procedure			
addition of syringe standard			
time of injection			

Addition of Extraction Standards to Sample Compartments:

$^{13}C_{12}$-Congeners	Concentration	Volume added to sample compartment [µl] :					total amount
	[µg/l]	condensate	filter	adsorbent	...	...	[pg]
2,3,7,8-TCDF							
2,3,7,8-TCDD							
2,3,4,7,8-PeCDF							
1,2,3,7,8-PeCDD							
1,2,3,4,7,8-HxCDF							
1,2,3,6,7,8-HxCDF							
2,3,4,6,7,8-HxCDF							
1,2,3,4,7,8-HxCDD							
1,2,3,6,7,8-HxCDD							
1,2,3,4,6,7,8-HpCDF							
1,2,3,4,6,7,8-HpCDD							
OCDF							
OCDD							

Addition of syringe standard to concentrated sample extract

volume of sample extract:		µl	
$^{13}C_{12}$-Congeners	Concentration	volume applied	amount
	[µg/l]	[µl]	
1,2,3,4-TCDD			
1,2,3,7,8,9-HxCDD			

End of table "Extraction & Clean.up"

Analytical Results

Equipment used (columns, mass spec):

Flue gas sample No.

Date of sampling

Flue gas sample volume [m³] dry gas at standard t, p and operational O_2/$CO_{2)}$

	PCDD/PCDF in flue gas *)		ng I-TEQ/m³		
indicator 2)	[ng/sample]	[ng/m³]	incl. DL	incl. 0.5 DL	excl. DL
Dioxins:					
Sum of TCDD 1)					
Sum of PeCDD 1)					
Sum of HxCDD 1)					
Sum of HpCDD 1)					
OCDD					
Total PCDD					
2,3,7,8-TCDD					
1,2,3,7,8-PeCDD					
1,2,3,4,7,8 HxCDD					
1,2,3,6,7,8-HxCDD					
1,2,3,7,8,9-HxCDD					

Recovery rates

Sampling standard		
	Recovery [%]	Remarks
1,2,3,7,8-PeCDF		
1,2,3,7,8,9-HxCDF		
1,2,3,4,7,8,9-HpCDF		
Extraction standard		
	Recovery [%]	Remarks
2,3,7,8-TCDF		
2,3,7,8-TCDD		
2,3,4,7,8-PeCDF		
1,2,3,7,8-PeCDD		
1,2,3,4,7,8-HxCDF		
1,2,3,6,7,8-HxCDF		
2,3,4,6,7,8-HxCDF		
1,2,3,4,7,8-HxCDD		
1,2,3,6,7,8-HxCDD		
1,2,3,4,6,7,8-HpCDF		
1,2,3,4,6,7,8-HpCDD		
OCDF		

ANNEX 2

Summarising report on PCDD/F emission measurements

NOTES FOR USE

This file contains the standardised form for final reporting of the results of dioxin emission measurements within the DGXI/LUA European Dioxin Project.

All results of emission measurements obtained at one particular installation shall be summarised within one file; thus, different installations require separated files.

This way of reporting was chosen to make writing of the report as convenient as possible. Just use the “tab keys” to move from field to field.

Since a number of data requested in the form may be identical throughout all measurements (e.g. data of calibration test gases etc.), the following procedure is recommended:

- Make a copy of the original file, named e.g. “fin_ rep_ master.doc”
- Insert all data which were not changed throughout your measurement campaigns into this master file. Save the master file.
- Make copies of the master file for each final report needed (one per installation); use file names which indicate the installation and the country (e. g. “Fin_ rep_ sinter1_ B.doc”)
- Fill in all data specific for the installation and the respective measurement campaign.

IMPORTANT: Do not use the form assistant of Microsoft Word to make any changes of the Form. In case you disclose the form, all data typed in so far will be lost when the form is protected again! If there is the need for additional information which cannot be inserted in the form please mail separately.

ANNEX 2

Summarising report on PCDD/F emission measurements

Report on PCDD/F Emission Measurement Carried Out Within the DGXI European Dioxin Project

1. General

Title:
Report on PCDD/F Emission Measurements at a Facility for

insert plant/facility type
in
Select country from list

Name(s) and location of involved institute(s):

Sampling:
....

Analysis:
....

Internal reference number of report: ....
Date of report: ....

Plant Operator:
☐ confidential ....

Plant Location
☐ confidential ....

Date(s) of Measurements:

Sample code	Day	Sample code	Day	Sample code	Day
....	dd.mm.yyyy	....	dd.mm.yyyy	....	dd.mm.yyyy
....	dd.mm.yyyy	....	dd.mm.yyyy	....	dd.mm.yyyy
....	dd.mm.yyyy	....	dd.mm.yyyy	....	dd.mm.yyyy

This report comprises ☐ Pages and ☐ Attachments

Summarising report on PCDD/F emission measurements

2. Description of plant/facility; handled materials

2.1 Type of plant/facility
(copy from first page)

2.1.1 Corresponding SNAP of CORINAIR CODE
e. g. 03 03 01

2.2 Description of plant/facility
(short description of plant and technical processes applied. Parts of the facility which are of special importance for the generation of PCDD/F shall be highlighted. Year of installation and of recent upgrade/modification. Details on absolute and specific capacity (related to products and/or input materials) shall be given)
....

ANNEX 2

Summarising report on PCDD/F emission measurements

2.3 Emission source

2.3.1 Stack data:
2.3.1.1 height above ground (m)

2.3.1.2 construction details

circular ☐ diameter bottom (m): ☐ diameter top (m)

rectangular ☐ length of side a (m): ☐ length of side b (m):

material: ....

2.3.1.3 stack cross section at top (m²):

2.4 Input materials according to license

....

2.5 Operation periods (hours)
daily: ☐ weekly: ☐ annually:

2.6 Waste gas collection and cleaning systems

2.6.1 waste gas collection system:
....

2.6.2 technical data of ventilator/suction device (if installed)
....

2.6.3 suction area (m²)
....

2.6.4 emission abatement system
(description of components as arranged downstream)

Summarising report on PCDD/F emission measurements

---

3. Position of the access port used for the measurement

(before/at stack, length of straight duct before access port, duct diameter at sampling point)

....

4. Instruments used for measurements, analytical procedures

4.1 Determination of flue gas conditions

4.1.1 Flue gas velocity

☐ Prandtl probe/micromanometer
☐ differential pressure gauge
☐ electronic micromanometer
☐ anemometer
☐ taken from operational data (i. e. ventilator)
☐ other (specify)

4.1.2 Static pressure in stack

☐ U-type manometer
☐ manometer as used according to 4.1.1
☐ negligible (< 0.005 hPa)

4.1.3 Ambient air pressure at access port

☐ barometer, type: ....
recent calibration on (date)

4.1.4 Flue gas temperature

☐ thermoresistor (type)
☐ Ni-Cr-Ni thermoelement (type)
☐ Hg-Thermometer (type)
☐ other devices (type)

Flue gas temperature was measured continuously at representative point in the stack; the measured values were

☐ registered continuously on paper
☐ registered continuously by electronic data logger/PC
☐ converted into half-hour averages

4.1.5 Moisture in flue gas

☐ Adsorption (followed by gravimetric determination) at
  ☐ silica
  ☐ calcium chloride
  ☐ other agent: (type)
☐ moisture measuring instrument for gases: (type)
☐ Psychrometer
☐ test tube (type, agent)

4.1.6 Density of flue gas

calculated from flue gas compounds as listed in the tabular reports (see ANNEX)

Summarising report on PCDD/F emission measurements

4.2 Gaseous and vaporised compounds

4.2.1 Continuous measurements

4.2.1.1 Compound	4.2.1.2 measuring principle	4.2.1.3 Producer, type	4.2.1.4 measuring range (dimension)	4.2.1.5 test gas used for calibration*)
Oxygen				(conc.) (date) (months)
carbon monoxide				(conc.) (date) (months)
carbon dioxide				(conc.) (date) (months)
(other compound)				(conc.) (date) (months)
(other compound)				(conc.) (date) (months)
(other compound)				(conc.) (date) (months)

*) please insert concentration, date of preparation, guaranteed period of stability (months)

Additional Remarks:............

4.2.1.6 Sampling/measuring line

Component	**heated/cooled to (°C)**	**length [m]**	**Material**
Sampling probe			
dust filter			
Sampling line before gas cooling/drying system			
Sampling line after gas cooling/drying system			
gas cooling/drying system			

4.2.1.7

90% response time of entire sampling system: .... seconds

determined by *(describe procedure)*

....

Summarising report on PCDD/F emission measurements

4.2.2 Discontinuous measurements

Compound: **Polychlorinated dibenzo-p-dioxins and dibenzofurans**

Sampling system and analytical procedure as described in the tabular reports (ANNEX)

5. Operation condition of the plant during measurements

5.1 Production facility:

type of operation *(e. g. charging, start-up, representative conditions, special condition relevant for emissions)*

…………

throughput/power
…………
Input materials
…………
products
…………
characteristic operation parameters *(e.g. pressures, temperatures)*
…………
deviations from licensed operation
…………

5.2 Flue gas cleaning system

Operation parameters for each device *(e.g. electric power, pressure, pH,)*
…………
temperatures *(thermal post combustion, scrubber, catalyst)*
…………
parameter influencing the emissions:
(e.g. interval of maintenance, pH, temperatur of post mbustion,operation time of catalyst)
…………
specialities of the system *(self-constructed parts, additional measures)*
…………
deviation from normal operation as described under 2.6.4
…………

---

6. Summary of results and discussion

6.1 Assessment of operation conditions during measurements

(special, unforeseen events?)

....

6.2 Results of measurements

Sample code	actual O_2 concentration [vol %]	PCDD/F [ng I-TEQ/m³]	reference O_2 concentration [vol%]	PCDD/F at ref. O_2 [ng I-TEQ/m³]

7 **Comments on results**:

....

Signature of responsible scientists/technicians: